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A DETERMINATION OF THE WAVE-LENGTH OF THE Kα LINE OF CARBON

By B. B. Weatherby

Abstract

A simplified type of vacuum spectrometer utilizing a plane glass grating with 250 lines per mm was used to measure the wave-length of the $K\alpha$ line of carbon. A water-cooled metal x-ray tube with tungsten cathode was connected directly with the spectrometer without the interposition of any absorbing screen in the x-ray beam. The measurements were made under varying conditions. The angle of incidence being varied from 20′ to 50′ and the distance from grating to plate from 50 cm to 80 cm. A weighted mean of all determinations gives the wave-length of the $K\alpha$ line of carbon as 45.4A.

Introduction

WITHIN the last year the extension of the diffraction grating method to soft x-rays has led to the measurement of a number of soft x-ray wave-lengths. The region investigated lies in the gap previously existing between the soft x-rays and the extreme ultra-violet. The gap between 27A and 136A has been worked on by Hunt[1] and by Thibaud,[2] using the plane grating, and by Osgood[3] using a concave grating. Dauvillier[4] using a fatty acid crystal has also made some measurements in the same region. The theory of using a line grating at grazing incidence with the x-rays striking within the angle of total reflection was first given by A. H. Compton.[5]

Unfortunately the results obtained by the investigations above referred to are not concordant, a variation of from 0.2A to 2A occurring on some of the lines. The wave-length of the $K\alpha$ carbon line, for example, varies from 43.96A according to Osgood to 46.0A according to Hunt. Dauvillier obtained 45.5A while Thibaud gives 44.9A. Since, because either of grease vapors or residual gases, this line appears on nearly all plates irrespective of the material of the cathode or anti-cathode, it makes a very good line to be used for reference or standardization purposes. It therefore seemed advisable to determine with some care the wave-length of the $K\alpha$ carbon

[1] Hunt, Phys. Rev. **30**, 227 (1927).
[2] Thibaud, Phys. Zeits. **29**, 241 (1928).
[3] Osgood, Phys. Rev. **30**, 567 (1927).
[4] Dauvillier, Jour. d. Physique **8**, 1 (1927).
[5] A. H. Compton, Phil. Mag. **45**, 1121 (1923); Proc. Nat. Acad. Sci. **11**, 598 (1925).

line. This has been done with a new form of vacuum spectrometer as a preliminary to a more extended investigation and is reported in this paper.

Apparatus

The apparatus is shown in Fig. 1. A brass tube 120 cm long and 11 cm in diameter was threaded at both ends. A brass cap *C* was screwed on one end and then waxed, while to the other end was fastened an ordinary T-casting *A*. The whole was then silver-plated to help prevent the emission of occluded gases. Both cathode and anti-cathode were fastened to the center of brass disks which were sealed to the side arms of the T with wax. The anticathode of copper was internally water-cooled. The angle on the face was about 10°. The cathode was made of heavy copper tubing and had a current-carrying capacity of 25 amps. It was externally water-cooled. A shield *B* was affixed to the cathode in order to place the first slit in the optical shadow of the filament. A heavy tungsten filament using about 15 amps. was placed 1 cm from the anti-cathode. Oxide filaments were tried but were discarded because the coatings disintegrated too rapidly under the

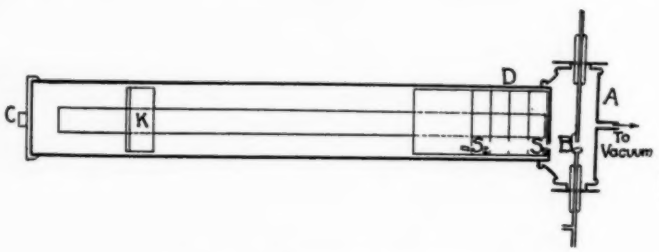

Fig. 1. Diagram of apparatus.

positive ion bombardment. The voltage for the x-ray tube was obtained from a 2000 volt d.c. generator. Transformers giving a R.M.S. voltage of 4400 were also used but did not give any better results than the generator and caused trouble by producing arcs in the tube.

The whole apparatus was evacuated by two stages of mercury diffusion pumps backed by a rotary oil pump. A vacuum of 0.0002 mm could be maintained during the operation of the x-ray tube.

An optical bench, one meter long, of heavy steel was made to carry the elements of the spectrometer. This was inserted at the *C* end of the apparatus. The front platform *D* carried the slit system and the grating. The distance apart of the slits was 18 cm. The slit width was adjustable being usually from 0.2 mm to 0.3 mm. The slit S_1 fitted snugly against a brass disk, with a rectangular opening in it, which closed the end of the spectrometer tube. There was a system of diaphragms between S_1 and S_2 to exclude visible light from the spectrometer.

The grating was mounted immediately behind the second slit. It could be adjusted and locked in any position. The grating was of glass and had 250 lines per mm. The constant was measured using the 5461A line of

mercury. This determination was certainly more accurate than the rest of the experiment. The aperture of the grating was 5 mm and it was ruled up to each edge. Larger aperture gratings were tried but had a tendency to broaden the lines and to make the location of the effective center of the grating more difficult. The angle of incidence varied from 25′ to 50′. The plate holder K could be moved along the platform and clamped in any position. It consisted of a light-tight box with a hinged iron lid on the front. The lid could be raised or lowered by means of an electromagnet outside the tube, an arrangement permitting the tube to be cleaned without fogging the plate. Distances from grating to plate of from 50 to 80 cm were ordinarily used.

Several kinds of plates were tried. Oiling of the plates was found unnecessary. Eastman Kodak Co. No. 36, a fairly fast plate, was found to be most satisfactory. Contrast plates with contrast developer gave less fogging but also less line intensity.

Procedure

The ordinary formula $n\lambda = D(\sin i \pm \sin\theta)$ used for the plane grating may be modified to $n\lambda = D\alpha(\alpha + 2\theta)/2$ for tangent incidence. Since that portion of the direct beam passing by the grating and also the reflected beam are of considerable width care must be exercised in the method of measuring the plate. Suppose in Fig. 2 that AC represents the width of the direct beam

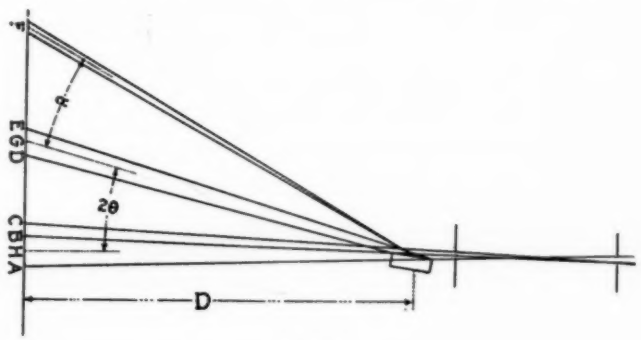

Fig. 2.

in the absence of the grating. On interposing the grating, part of this beam is cut off and only the part BC will remain. The portion cut off by the grating will be reflected to DE and diffracted to F. The maximum width of the diffracted line for plate distances D up to 60 cm was 0.03 cm. Measurements were made to the center of this line. For the large plate distances the width of BC and DE became as great as 0.09 cm. Since it was necessary to measure the distances on the plate between direct, reflected and diffracted beam to at least 0.01 cm in order to obtain the wave-length within 0.2A the need for care in choosing the proper place in the direct and reflected beam from which to measure is evident.

An inspection of Fig. 2 will show that the portion of the direct beam AB which is cut off by the grating face is reflected to DE. The widths AB and DE are consequently equal. Thus the angle 2θ can be found by measuring the distance BE with a comparator since the edges of both the direct and reflected beam are sharp and since the distance D is known. The width of the reflected beam was also measured with a comparator. Both above measurements could be repeated to 0.001 cm.

The distance D was measured from the center of grating to the plate. Since the grating had a 0.5 cm aperture the maximum error in the measurement of this distance for $D=50$ cm was 1/2 percent. Obviously this percentage was less for the greater distances. The percentage error in D was probably considerably less than this since an error of 1/2 percent assumes that the effective "center" of the grating was at either of the two edges.

The angle α was measured from the center of the reflected beam to the center of the diffracted. Whenever possible this was done with a comparator. Frequently, however, the diffracted lines were too weak to stand the magnification of the comparator. In these cases the plate was fastened to a glass scale etched to 0.1 mm and the image of the one superimposed on the other was thrown on a screen by a projection lantern. This made a convenient method for measuring the distance GF to within 0.01 cm. The error in the computation of each plate by the above method of measurement should not be in excess of 0.2A. The mean value of a group of plates under varying conditions should give a wave-length value even closer than this.

Results

While other lines (several of which have been measured) appear on many of the plates beside the $K\alpha$ carbon line, they are not reported on in this paper. The iron line appears frequently. This is no doubt due to the use

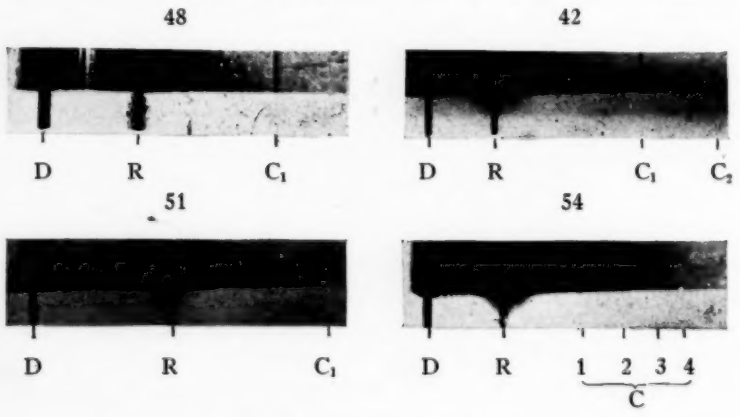

Fig. 3. Reproductions of spectra.

of steel screws for holding the hot filament in place. Although a copper anti-cathode was used, the copper lines do not appear on the plate. The copper wave-length is so short (13.3A) that it would fall in that portion of

the plate fogged by visible light. Moreover, after a short time the anti-cathode was covered by a film of tungsten and other impurities. A covering of graphite was placed on the anti-cathode but did not increase materially the intensity of the carbon lines. In this work the carbon line always appeared if there was any other line present.

Exposures of as long as six hours were used for the large plate distances. With a plate distance of 30 cm from two to three hours sufficed. The usual plate current was about 40 milliamps. although this was run up to 90 milliamps. occasionally.

In Fig. 3 reproductions of plates No. 42, 48, 51, 54 are shown. The originals naturally show more detail than the reproductions. In the plates shown the lower half of the field was covered by carbon paper. There is a noticeable scattering and broadening of the x-ray beam on some of the plates due to this. However, on practically all the original negatives it was possible to locate the edges of the direct and reflected x-ray beams in the upper portion of the plate where the direct and reflected light appears. The lines on the plates taken with $D = 80$ cm were too weak for reproduction but could be measured.

Table I gives the operating conditions for each of the plates. They were all taken with 2000 v. on the anti-cathode.

TABLE I. *Operating conditions for each plate*

Plate No.	D (cm)	θ^1	Exposure (hrs)	Plate Current (milliamps)	λ	Weight
42	50	33	3	45	45.2	3
43	50	33	3	35	45.3	1
44	81	30	5	40	45.4	2
45	81	32	6	55	45.5	1
46	50	33	3	40	45.4	2
47	50	27	3	40	45.4	2
48	50	45	4.5	45	45.5	2
50	60	51	5.5	25	45.4	3
51	60	51	6	50	45.3	3*
52	60	25	6	55	45.5	3
54	30	60	3	45**		

* Transformer at 4400 V.
** Plate distance too small to make accurate calculation.

A weighted mean of 11 observations give the value of the wave-length of the $K\alpha$ carbon line as 45.4A. The weights were assigned by giving those with the greater plate distances wider dispersion and finer lines a value of 3 and the others a value of 2 or 1 depending on how they met the above conditions.

In conclusion, the author wishes to express his thanks to Dr. C. B. Bazzoni under whose direction this work was undertaken and carried through and who has given several valuable suggestions.

RESEARCH SECTION RANDAL MORGAN LABORATORY OF PHYSICS,
UNIVERSITY OF PENNSYLVANIA,
July, 1928.

TOTAL REFLECTION OF X-RAYS FROM NICKEL FILMS OF VARIOUS THICKNESSES

By Hiram W. Edwards

Abstract

The total reflection of x-rays ($\lambda = 0.707$A) is obtained from mirrors of sputtered nickel films having thicknesses from 0 to 3.3×10^{-4} cm. The measured critical angles were found to vary from a minimum value of 0.0016 radians, that of blank glass, to a maximum value of 0.00339 radians, which was obtained from the thickest nickel film. A satisfactory agreement between the maximum experimental value of the critical angle and that calculated by the Lorentz dispersion formula in which the density of nickel was placed at 8.75 gm/cc, is used as evidence for concluding that the density of the nickel is entirely normal and also that the thickness of sputtered metal films which are to be used in x-ray reflection phenomena must be sufficiently large or misleading results may be obtained. The critical angle from a thick silver sputtered mirror was found to be identical with that obtained from a chemically prepared silver mirror which indicates that the density of silver is independent of the method of deposition.

THE total reflection of x-rays from flat surfaces of glass, quartz and from metals has been investigated by several individuals.[1] From measurements made of the critical angles from these surfaces the index of refraction for x-radiation of differing frequencies has been determined. It has also been shown that the Drude-Lorentz dispersion formula may be used for calculating the index of refraction provided that the frequency of the incident radiation is not close to the critical absorption frequency limits of any of the electrons in the reflecting surface.

In a recent article,[2] Stauss describes his work with sputtered films of nickel, silver and platinum, and gives results from which he concludes that the densities of the nickel and platinum in the sputtered films must have values (4.13 and 5.44 gm/cc for nickel and 14.1 gm/cc for platinum) which are far below their normal values. In partial corroboration with these results he refers to the work of Hanawalt and Ingersoll[3] who report an increase in the lattice constant of nickel in nickel sputtered films, and hence, a decrease in the density. The results of Hanawalt and Ingersoll are not quantitatively in agreement with those of Stauss.

The writer has undertaken to measure the critical angles of several nickel sputtered films which were prepared so that the thickness of the films ranged from a very small value to one of considerably greater value. The amount of metal upon the thinnest film was so little that it was scarcely noticeable on the flat glass surface. The thickest film was entirely opaque to intense sources of visible light.

[1] Compton, Phil. Mag. **45**, 1121 (1923); Linnik and Loscharew, Zeits. f. Physik **38**, 659 (1926).

[2] Stauss, Phys. Rev. **31**, 491 (1928).

[3] Hanawalt and Ingersoll, Nature **119**, 234 (1927).

The critical angle for each film was measured by an x-ray reflection apparatus, a description of which appears elsewhere.[4] In this apparatus very long optical paths were provided which reduced the errors in determining the critical angle to values which are less than one percent.

The radiation used was from a water-cooled molybdenum tube which was operated at about 45000 volts. The $K\alpha$ lines were sufficiently intense in comparison with the general radiation to render unnecessary the use of a crystal for providing monochromatic radiation.

The experimental values of the critical angles from the several nickel films together with the one from an unsputtered glass mirror, are tabulated below. The films were all sputtered in air as a residual gas. For the sake of indicating the relative thicknesses of the films the duration of the sputtering time (in minutes) is included. The conditions under which the sputtering took place were maintained as nearly constant as possible, and hence one may assume that the deposit of metal was proportional to this time of sputtering. The thickest of the films was weighed with a probable error of about 10 percent.

TABLE I. *Variation of Critical Angle with Surface Density of Nickel Films.*

Mirror No.	Time of Sputtering (min.)	Critical Angle (radians)	Surface Density (mgm per cm^2)
1	0	0.00160	0.0
2	10	0.00266	0.036
3	15	0.00272	0.054
4	30	0.00308	0.101
5	45	0.00333	0.163
6	80	0.00339	0.290
Calculated value from dispersion theory		0.00340	

Using the Drude-Lorentz dispersion formula, assuming that the density of the nickel was 8.75 gm/cc (which is an average of the values 8.6 and 8.9 given by the Handbook of Chemistry and Physics, published by the Chemical Rubber Publishing Co.) and including the critical $K\alpha$ absorption frequencies for the K electrons, a value of 0.00340 radians was obtained, which is in good agreement with the value obtained by experimentation when using the thickest film. Even if one uses either extreme limit of the values of the density given above the disagreement is not over 1.5 percent. For a density of 8.6 the calculated value of the critical angle is 0.00336 and for 8.9 the value is 0.00344 radians.

These results do not give absolute proof that the density of the nickel in the thinnest film is not the same as it is in the thickest film, but it would seem that a far more reasonable explanation of the smaller values obtained for the critical angles from these films is that the phenomenon of the total reflection of x-rays is not a superficial effect but rather requires a layer of electrons of a somewhat definite thickness. If this is the case, reflection from

[4] Edwards, Phys. Rev. **30**, 91 (1927).

the thin films is dependent not only upon some of the electrons of the nickel film, but also upon some of the electrons of the constituent atoms of the glass below the nickel film. The increase of the critical angle with increased thickness of the nickel film supports this hypothesis. The very small change in the critical angle determined by the last two films, even though the film on No. 6 must be nearly twice as thick as that of No. 5, shows that the addition of still more nickel would not measurably change the final result. This statement is substantiated by the agreement of the calculated value with the final experimented value. These results strongly indicate that the actual density of the nickel does not have different values in films of different thicknesses.

The close agreement between the final value of the critical angle and that obtained from the dispersion formula also indicates that actual density of the nickel in the sputtered films used cannot differ by more than 1 percent from the value of 8.75 as used in the theory. Hanawalt and Ingersoll's results indicate an increase in the lattice constant of crystallized nickel in the film of 20 percent and less. Some of their first results indicated that the nickel was not crystalline but amorphous. It is hard to reconcile these two contradictory results.

Some difficulty was encountered in determining the mass of the nickel deposited upon the glass receiving surface. The final method used which gave satisfactory results employed a glass counterpoise which was nearly equal in mass to that of the receiving glass. The glass counterpoise was placed in the sputtering chamber directly under the receiving glass in order to insure a similar treatment, except for the deposit of nickel. The surface density of the nickel on mirror No. 6 was found to be 0.29 mgm per sq. cm.

From the above value of the surface density of nickel, together with a volume density of 8.75 gm/cc the thickness of the nickel film on mirror No. 6 was calculated to be 3.32×10^{-5} cm, which is a little shorter than the shortest wave-length of the visible spectrum. The distance of effective penetration of the x-radiation into the nickel film was found to be 0.00975 cm, assuming that the radiation followed the direction of the line of incidence.

The writer has also measured the critical angle from two different silver films, one of which was deposited upon glass by a chemical method (using the reduction of a silver salt) and the other a sputtered film upon glass. Both films were entirely opaque to ordinary light. The measured critical angles were identical in the two cases and both agreed, within one-half percent, with the value calculated by the dispersion formula. There is undoubtedly no change of density of silver in sputtered silver films.

UNIVERSITY OF CALIFORNIA AT LOS ANGELES,
July 31, 1928.

THE SPECTRA OF MERCURY ABOVE THE IONIZATION POTENTIAL

By L. R. Maxwell*

Abstract

Excitation of arc spectra of Hg by electrons having velocities above the ionization potential. Effect of recombination.—Electrons in mercury vapor with velocities greater than the ionization potential were confined into a beam by a magnetic field. The light produced was projected on the slit of a spectroscope with the direction of the beam at right angles to the slit. Perpendicular to the beam an electric field withdrew positive ions before they recombined. The intensity of the arc lines was found to be independent of the electric field which indicates that recombination contributes very little to the formation of these lines. These results are contrary to the previously accepted explanation given for the complete arc spectrum appearing above the ionization potential. Consequently in addition to simple excitation the arc spectrum can be explained in the two following ways, (1) as being due to the return to the 1^1S_0 state by an electron which has been displaced from an inner energy level to a virtual orbit while simultaneously one of the electrons of the valency group falls in to fill the vacated level; (2) due to a special type of recombination which is called initial recombination.

Intensity variation of the spark lines due to the motion of the positive ions.—Spark lines due to singly and doubly charged ions show a variation of intensity along their length in such a manner that it is possible to distinguish them from the arc lines. It is also possible to differentiate between the lines of the first and the second spark spectrum.

SINCE the complete arc spectrum of the normal mercury atom appears when the mercury vapor is ionized it was formerly supposed to be due to the ionization of the gas or rather due to the recombination of the free electrons with the atomic ions. However, Eldridge[1] has found that important lines of the arc spectrum can be produced below ionization which is in accord with the Bohr theory and in agreement with the photoelectric experiments of Franck and Einsporn. In previous experiments on the spectrum of mercury vapor excited by the higher velocity electrons, effects due to the direct impacts and to recombination have not been separated. The question arises as to which of these processes contributes the more to the production of the arc lines. The purpose of this work is to obtain the mercury spectrum with and without recombination occurring and to determine the role which recombination plays in the production of the arc lines and also to study some of the characteristics of the mercury spark spectrum given out by ions having a particular direction of motion.

Experimental Arrangement and Procedure

In Fig. 1 is shown the arrangement of electrodes which were mounted in a bulb containing mercury vapor at a pressure of 0.001 mm of Hg. Elec-

* National Research Fellow.

[1] John Eldridge, Phys. Rev. **23**, 685 (1924).

trons from the heated tungsten filament F were accelerated through the slit system S_1 with velocities greater than 40 volts. The electrons passed through the opening in S_2 and were given an additional velocity which carried them into the Faraday cage C. The purpose of the field between S_2 and C was to prevent the return of secondary electrons from C. The filament was a straight wire whose cross section is shown at F. A uniform magnetic field of several hundred gauss produced by Helmholtz coils was in the direction indicated at H and served to confine the electrons into a well defined beam. The light coming from the region indicated by the dotted circle was projected on the slit of the spectroscope in such a manner that the direction of the beam was perpendicular to the slit. An electric field parallel to the slit placed between the two parallel plates served to withdraw the ions before they recombined. This field was not made greater than 200 volts per cm. It can be shown that when the electrons are under the influence of this transverse electric field they will not be deviated appreciably from their original path and that their velocity will not be altered by more than a fraction of a volt. The positive ions on the other hand will be drawn over to the plate while their path will describe an arc of a cycloid of very large diameter compared with the dimensions of the apparatus, that is, the ions will move practically in a straight line in going to the plate. Galvanometer G_2 gave a measure of the current reaching the edges of S_1. This was small compared to the total current of the beam collected by C as measured by G_6. G_5 indicated a small number of scattered electrons which reached S_2. Either G_3 or G_4 could be used for measuring the positive ion current. The region midway between the parallel plates which was occupied by the beam was kept at the same potential as S_1 and S_2. The two parallel plates were kept positive and negative respectively by the same amount with reference to S_1, S_2. Without this cross field we have the electrons moving in a region free from external electric fields and hence the ions and free electrons are able to recombine. The procedure was to apply an electric field of such an amount that a saturation positive-ion current was obtained, so that every ion formed was removed before it was allowed to recombine. Photographs of the spectrum were taken with and without the cross field applied.

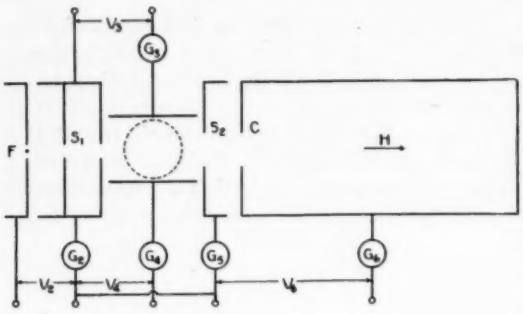

Fig. 1. Diagram of apparatus.

Experimental Results and Discussion

Fig. 2 shows a typical plate. The velocity of the electrons in this case was 300 volts. The top exposure was taken with the cross field applied and

the lower one without. Beneath the lines indicated by the circles are spark lines (2847A, 2947A, 3208A) classified by L. and E. Bloch[2] as due to singly charged ions and called by them E_1. The dots mark lines of the second spark

Fig. 2. Spectra of mercury (1) with the cross field applied and (2) without. The direction of motion of the positive ions is given by the arrow.

spectrum which have been designated as E_2 by L. and E. Bloch. One of them (4797A) can easily be seen while the others are very much fainter but could be readily observed on the original negative. The other lines belong to the arc spectrum. Some of them such as the one indicated by the cross (which is the 2537A line) are much longer than the others and actually extend beyond the region of the beam. The light coming from the part outside the beam is thought to be due to resonance radiation.

It is noticed that the arc lines and the lines of the first spark spectrum are unaffected by the field while the lines due to the doubly charged ion show a change in their intensity distribution. Curve 1 in Fig. 3 shows more clearly the intensity of the 4797A line with respect to the beam. On the ordinate is plotted intensity in arbitrary units and on the abscissa the position with respect to the center of the beam. Curve 2 represents one of the arc lines belonging to the sharp series which showed but little resonance radiation and gives the variation of the electron current in the beam. The direction of motion of the ions is indicated by the arrow and it is seen that the spark line is actually displaced in this direction.

By altering the size of the filament and the openings in the diaphragms a beam of much greater width could be produced so that the ions in their

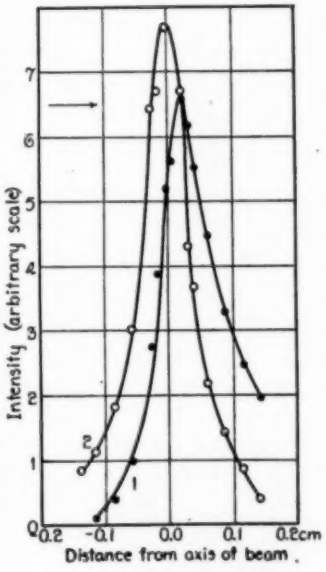

Fig. 3. Experimental curves showing intensity variation of (1) the 4797A line of Hg^{++}, and (2) an arc line which gives the width of the beam.

[2] L. and E. Bloch, Jour. d. Physique **4**, 333 (1923).

journey through it would be more apt to experience a second collision. The photographs obtained show the arc lines still unchanged in the presence of the electric field, but the lines of the singly charged ions now exhibit a change in intensity as is shown by Curve 1 in Fig. 4. Curve 2 represents the intensity for an arc line which gives the width of the beam. As to whether these E_1 spark lines show a change in intensity because of the electric field

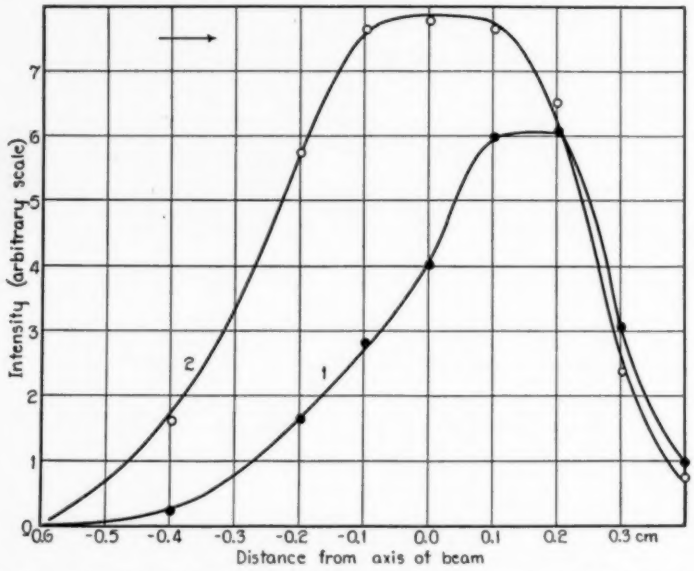

Fig. 4. Experimental curves showing intensity variation of (1) the 2847A line of Hg^+ and (2) an arc line which gives the width of the beam.

is found to be determined by the size of the beam. We are led to believe that the light observed with the wider beam is due to a double collision while that of the other is brought about by a single impact. Since the arc lines are always unaffected by the external field we are able by suitably adjusting the size of the beam to distinguish between the spark and arc spectrum and also are able to differentiate between the spark lines of the first and second spark spectrum.

Fig. 5. Showing two exposures taken close together on the same plate with and without the cross field.

Fig. 5 shows two exposures taken on the same plate with and without the cross field. The line beneath the dot which is the 4797A E_2 line shows the effect of the field. The densities of the other lines which belong to the arc spectrum were found to be the same for the two exposures. We therefore conclude that recombination does not contribute to the production of the arc spectrum under the conditions of this experiment, since recombination would be much less effective with the electric field than in its absence. The electron current in the beam was of the order of 10^{-4} amperes/cm^2 while the positive ion current was 10^{-5} amperes/cm^2. The electron current and the pres-

sure in the tube could be kept constant over a period of four hours which was the time necessary for the two exposures. For testing the constancy of conditions two photographs were taken with all conditions the same and the density of the lines were found to be equal.

Recently Mohler[3] has shown that recombination spectra do occur but he found it necessary to use high concentrations of ions and slow electrons. As is to be expected he found continuous bands terminating sharply on the high wave-length side. Thus to obtain spectra due to recombination a relatively large number of ions and slow electrons must be assembled together.

Having now definitely shown that in this experiment recombination does not occur of sufficient amount to account for the formation of the arc lines it is necessary to resort to collision processes to explain their existence. Since the velocity of the electrons is of the order of 200 volts it has much energy in excess of that which it would be necessary for it to lose in order to excite only the arc spectrum. Eldridge[4] has shown, on measuring the energy losses at electron impacts, that in mercury vapor when the electron has a velocity slightly above 4.9 volts it is then most likely to lose that amount of energy, but when it is increased to 16.5 volts very few electrons suffer this energy loss. This experiment as well as others has shown that the efficiency of excitation for these small velocities reaches a maximum slightly above the critical potential and then decreases, so that if the curve representing probability of excitation, were extrapolated to the higher velocities it would indicate that 200 volt electrons would not be likely to lose only these small amounts of energy. We should therefore not expect that these high velocity electrons would be able to produce the arc spectrum by simple excitation. The experiments of Bricourt[5] and also Seeliger in which the intensity of lines of the arc spectrum have been measured as a function of the velocity of the electrons, show that the intensity of the light starting sharply from the threshold value reach a maximum and then decrease as would be predicted by the experiments on the efficiency of excitation. Their results also give that the light intensity increases again for the higher velocities to a second maximum which is about equal to the first and comes at about eighty volts. It seems reasonable to suppose that this second rise of the curve is due to the appearance of a new phenomenon in which the electrons of the filled inner groups play a part.

Fricke[6] and others in measuring x-ray absorption have shown that several of the absorption limits have a definite fine structure. Kossel[7] has accounted for this as being due to the transport of an electron from its shell to the periphery and to certain virtual orbits which lie outside of the atom. The amount of energy for the latter process is of course the greater and hence we find the lines of the fine structure appearing on the high frequency side of

[3] F. L. Mohler, Phys. Rev. **31,** 187 (1928).
[4] John A. Eldridge, Phys. Rev. **20,** 456 (1922).
[5] P. Bricourt, Comptes Rendus **185,** 846 (1927).
[6] H. Fricke, Phys. Rev. **16,** 202 (1920).
[7] Kossel, Zeits. f. Physik **1,** 124 (1920).

the absorption band. More recently Chamberlain and Lindsay[8] in determining outer x-ray energy levels for the elements from antimony to samarium have postulated three possible transition combinations which can be expected for antimony, tellurium and iodine, to explain the L_{I} absorption limit. (1) An electron ejected from the L_{I} orbit might go to infinity and a valence electron from the $O_{\text{II III}}$ group drop in to fill the vacated place. (The $O_{\text{II–III}}$ is for these elements what might be called the incompletely filled valency group.) (2) The L_{I} electron could stop in the $O_{\text{II–III}}$ level and then fall back again to its original level. (3) The electron ejected from the L_{I} level might go to a virtual orbit and then one of the electrons in the $O_{\text{II–III}}$ level drop back to fill the vacancy in the inner energy level while at the same time the electron in the virtual orbit falls back to the $O_{\text{II–III}}$ group. Processes analogous to (1) and (2) would not give out the arc spectrum while (3) by virtue of the electron going from the excited state to the normal valency level could emit lines of the arc spectrum. To explain the second maximum of Bricourt's intensity-voltage curve and to account for the production of the arc lines by the high velocity electrons in the present work, we suggest that transition combinations similar to (3) are taking place.

The formation of arc lines may be due to a special type of recombination which is called initial recombination. Formerly initial recombination was thought to be a recombination between two ions generated from the same molecule. According to this hypothesis an electron ejected from a molecule goes only a small distance from the ion. The electron, however, is still attracted to the ion and will return again to recombine unless there exist external fields of sufficient strength which can remove the electron completely from the ion. Recently Franck[9] has proposed an initial recombination which he describes as being a recombination between an ion and its own electron under the condition in which the electron is not free. He considers the process as not being appreciably affected by external fields because the electron is assumed to be always under the influence of the intense field of the ion. In the present investigation the external fields were not great enough to prevent initial recombination as defined by Franck and consequently the observed intensity of the arc lines may be due to this type of initial recombination.

The writer desires to express his thanks to Professor John T. Tate for proposing this method of producing spectra without recombination and to Professor W. F. G. Swann for his suggestions during the course of this work. Also the writer wishes to thank Professor James Barnes for the privilege of using the densitometer at Bryn Mawr College. The investigation was begun in the Physical Laboratory of the University of Minnesota.

BARTOL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, PA.
July 16, 1928.

[8] Chamberlain and Lindsay, Phys. Rev. **30**, 369 (1927).
[9] Franck, Jour. Franklin Inst. **205**, 473 (1928).

THE DETERMINATION OF THE MEAN LIFE FOR THE 4797A SPARK LINE OF DOUBLY IONIZED MERCURY

By L. R. Maxwell*

Abstract

With the method illustrated by the writer in the preceding paper, the spark line 4797A due to ions moving in a particular direction through a beam of electrons was obtained showing a peculiar variation of intensity. Calculations are made to determine how the intensity of the line should vary with respect to its position across the beam and for different current densities of the beam. Cases are worked out for both uniform and non-uniform electron current densities of the beam. On comparison with the experimental results, it can be shown that the line is produced at a single electron impact, and that the average life of the excited state is 4×10^{-7} seconds. Although the mean life for the first order spark lines could not be measured, it is estimated that it is less than 1×10^{-7} seconds.

IN THE preceding paper an experimental arrangement was shown for producing spark lines from positive ions which were all moving in a particular direction through an atmosphere of fast moving electrons. The spark lines of doubly ionized mercury showed a displacement in the direction of motion of the ions. This paper deals with a calculation of how the intensity of the line should vary across the beam and also with respect to the electron current density. As a consequence of these calculations a method is obtained for the determination of the average life of excited states which is applicable to any type of ion.

Case of Electron Beam of Uniform Current Density

Part I. *Single collision.* We shall now assume that the atom is ionized and excited at a single impact. In Fig. 1, the parallel lines M and N represent the boundary of the beam whose current density we shall assume to be uniform. The dimension perpendicular to the paper we shall assume to be constant and represented by p. When a positive ion is formed it immediately moves under the influence of the electric field in the direction indicated by the arrow at O. Let δn be the number of excited ions which will be formed per second in the volume element $dv=lpd\xi$. Then

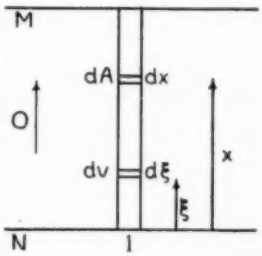

Fig. 1.

$$\delta n=\alpha N d\xi$$

where N is the number of electrons passing through unit cross sectional area per sec., $\alpha=lp/\lambda$ with λ being the mean free path for this type of collision.

We shall now determine how much light these δn excited ions will give off while they are passing through the volume element dA at a distance x from

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the lower edge of the beam. If we consider these ions radiating according to the ideas of classical dynamics the ion which has obtained its energy in the volume element dv will start to radiate immediately and if E_0 is the energy it had at the beginning, then the amount E which it still has left at the end of a time t is given by

$$E = E_0 e^{-t/\tau} \tag{1}$$

where τ is the mean life and is equal to $3cm\lambda^2/8\pi^2e^2$. λ is the wave-length of the light emitted, m and e are the mass and charge of the electron, and c the velocity of light.

According to the quantum theory the ion will not radiate continuously but instead will keep its energy for a certain length of time and then radiate all it has during a time interval small compared to its life. Thus we have that the number of excited ions n_t existing at any time t is given in terms of the initial number n_0 by

$$n_t = n_0 e^{-\beta t} \tag{2}$$

where the reciprocal of β is the mean life.

For all of the following calculations we will think of the process of radiation as one which obeys the ideas of the quantum theory. Since the algebraical form of the two above equations are the same we could select either of them and still arrive at the same result. In other words we will not be able to distinguish between the quantum and classical theories of radiation.

So that now, if δn is the number of excited ions leaving dv per second, then

$$\delta n e^{-\beta t(x,\xi)}$$

is the number which will arrive at a distance x from the lower edge of the beam. Where $t(x,\xi)$ is the time required for the ion to go from dv to dA, and

$$-d(\delta n) = \beta\alpha N e^{-\beta t(x,\xi)} d\xi dt$$

will give the number of transitions occurring in dA; where $dt = (dt/dx)dx$. If we let X be the external field then we shall assume that the ion moves under the action of this field so that

$$t(x,\xi) = [2m(x-\xi)/Xe]^{1/2}$$

where m/e is the ratio of mass to charge of the doubly charged ion, $-d(\delta n)/lpdx$ gives the number of transitions occurring per second per unit volume at position x due to those excited ions formed in dv. On assuming that the light intensity I per unit volume at x is proportional to the number of transitions occurring per sec. per unit volume at x we then have

$$dI = -\frac{Kd(\delta n)}{lpdx} = \frac{A\beta Nm \exp\left\{-\beta[2m(x-\xi)/Xe]^{1/2}\right\} d\xi}{Xe[2m(x-\xi)/Xe]^{1/2}}$$

where K is the factor of proportionality and $A = \alpha K/lp$. On integrating ξ from 0 to x we obtain

$$I = AN[1 - e^{-\beta(2mx/Xe)^{1/2}}] \tag{3}$$

Part II. *Double collision.* We now assume that at the first collision the ion is formed unexcited, then, as it is moving through the beam it is hit a second time which causes it to be put in the excited state. It will then radiate at a definite time later, after it has moved on to a new position. We will first find the number of unexcited ions formed in the volume element dv which are excited in $d\eta$ and then radiate in dA. Fig. 2 shows these elements of volume with their respective positions from the edge of the beam. The dimension perpendicular to the paper will be considered constant as before and will be represented by p.

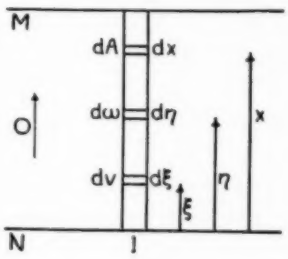

Fig. 2.

In the volume $dv=lpd\xi$ we have $\alpha' Nd\xi$ unexcited ions formed per second which we shall call δn_0. If in general we have δn unexcited ions passing through an atmosphere of fast moving electrons at any given time t then the number of these $-d(\delta n)$ which will become excited during a subsequent time dt will be directly proportional to N, δn, and dt. Thus

$$-d(\delta n)=\gamma N\delta n dt$$

where γ is the factor of proportionality.[1] Hence the number of unexcited ions coming from dv per second which will reach $d\omega$ without becoming excited will be $\delta n_0 e^{-\gamma N t(\eta,\xi)}$ where $t(\eta,\xi)$ is the time required for the ion to go from dv to $d\omega$. The number of these ions which will be excited in $d\omega$ is

$$\gamma N\delta n_0 e^{-\gamma N t(\eta,\xi)}[dt(\eta,\xi)/d\eta]d\eta$$

and the fractional part of this number which will be de-excited in the volume dA is

$$\beta\gamma N\delta n_0 e^{-[\gamma N t(\eta,\xi)+\beta t(x,\eta,\xi)]}\frac{dt(\eta,\xi)}{d\eta}\,\frac{dt(x,\eta,\xi)}{dx}d\eta dx$$

where $t(x,\eta,\xi)$ is the time taken for the ion to travel from $d\omega$ to dA. We shall again assume as above that the light intensity I per unit volume observed at x to be proportional to the rate at which transitions occur per unit volume at this position. Thus we obtain

$$I=A'\beta\gamma N^2\int_{\xi=0}^{x}\int_{\eta=\xi}^{x}e^{-[\gamma N t(\eta,\xi)+\beta t(x,\eta,\xi)}\frac{dt(\eta,\xi)}{d\eta}\,\frac{dt(x,\eta,\xi)}{dx}d\xi d\eta \qquad (4)$$

where $A'=\alpha' K/lp$. But

$$t(\eta,\xi)=[2m(\eta-\xi)/Xe]^{1/2}\,;\; t(x,\eta,\xi)=\frac{2(x-\eta)}{[2Xe(\eta-\xi)/m]^{1/2}+[2Xe(x-\xi)/m]^{1/2}}$$

on substituting these values, this equation becomes, after integrating

$$I=[A'/(N\gamma-\beta)][\beta N(e^{-N\gamma(2mx/Xe)^{1/2}}-1)+\gamma N^2(1-e^{-\beta(2mx/Xe)^{1/2}})] \qquad (5)$$

[1] It is here assumed that the velocity of the ions is small compared to the velocity of the electrons so that γ is constant.

This can be simplified if the exponential terms are expanded according to the exponential power series and if γ is considered to be small so that terms containing γ^2 can be neglected, so that it reduces to

$$I = \text{constant} \times N^2 \tag{6}$$

The significance of making γ small is that we are assuming that the probability of the ion being struck the second time is small.

Eq. (3) informs us that if the light is due to a single impact the intensity should always be directly proportional to the electron current regardless of what particular position on the line the measurements were made. However, if the emission were due to a double collision, Eq. (5) shows that the radiation is not a simple function of the current density and that the relative intensities will depend upon x. If the probability of the ion being struck the second time is small then the intensity is proportional to the square of the current. For very large values of x (3) and (5) become the same in that they give that I would simply be proportional to N.

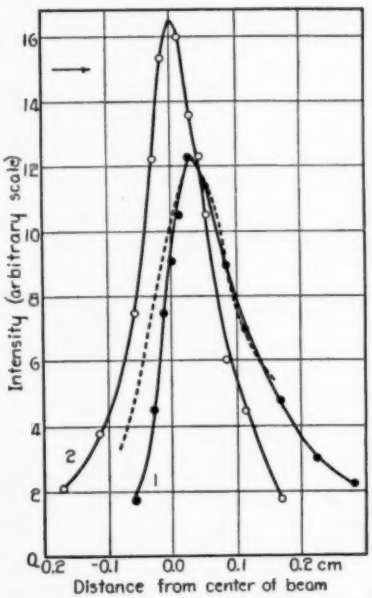

Fig. 3. Experimental curves showing intensity variation of (1) the 4797 spark line and of (2) an arc line which gives the width of the beam. The dotted line gives a calculated curve for (1) the spark line.

In Fig. 3 we have the experimental results of the intensity measurements. On the ordinate axis is plotted intensity in arbitrary units while the abscissa gives the position with respect to the center of the beam. Curve 2 is for an arc line which showed little resonance radiation so that it can be thought to show how the electron current density varies across the beam. The intensity of this line was found to be proportional to the electron current, so that it must be due only to single electron collisions and hence give a true measure of the electron density. Curve 1 represents the spark line 4797A of Hg^{++} which shows a displacement in the direction which the ions are moving as indicated by the arrow. The curve rises sharply at first to the maximum which has been displaced from the center of the beam and then falls off more gradually. The relative intensity of this line was measured for different electron currents and found to be approximately proportional to the electron density and to be the same for different values of x. If the electron density had been uniform it is immediately seen that the light is the result of a single collision and the constant β could be determined by using Eq. (3) and hence the mean life is obtained. By use of Curve 2 it can be estimated how 1 would have appeared if the current had been uniform and from Eq. (3) the mean life comes out to be of the order of 10^{-7} seconds.

However, to obtain a more accurate method we shall proceed to make similar calculations as above on the assumption that the electron current is similar to that shown by Curve 2.

Case of Electron Beam of Non-uniform Current Density

Part I. *Single collision.* We shall assume that the electron current varies as is shown in Fig. 4. That is, we assume $N=k\xi$ for values of ξ between zero and a, and $N=ka-k(\xi-a)$ for ξ from a to $2a$. This variation of N with respect to ξ is taken to represent approximately the actual condition as is given by Curve 2 of Fig. 3. Proceeding as above we obtain the following for the light intensity for values of x from 0 to a,

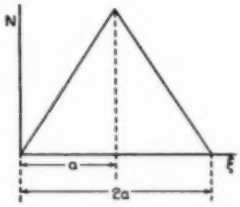

Fig. 4.

$$I=(A\beta m/Xe)\int_0^x k\xi[2m(x-\xi)/Xe]^{-1/2}e^{-\beta[2m(x-\xi)/Xe]^{1/2}}d\xi$$

and on integrating becomes

$$I=Ak\left[\left(x-\frac{Xe}{m\beta^2}\right)+e^{-\beta(2mx/Xe)^{1/2}}\left(\frac{Xe}{m\beta^2}+\frac{Xe}{m\beta}\left(\frac{2mx}{Xe}\right)^{1/2}\right)\right] \tag{7}$$

This gives the intensity up to the center of the beam and we see that by varying the electron density we simply alter k and hence I is directly proportional to k and the relative intensities are independent of x.

For values of x from a to $2a$, we have

$$I=\frac{A\beta m}{Xe}\left[\int_0^a \frac{k\xi e^{-\beta[2m(x-\xi)/Xe]^{1/2}}d\xi}{[2m(x-\xi)/Xe]^{1/2}}+\int_a^x \frac{(2ka-k\xi)e^{-\beta[2m(x-\xi)/Xe]^{1/2}}d\xi}{[2m(x-\xi)/Xe]^{1/2}}\right]$$

On integrating we obtain

$$\begin{aligned}I=Ak\Bigg\{&a+\frac{Xe}{m\beta^2}-x'+e^{-\beta[2m(a+x')/Xe]^{1/2}}\left(\frac{Xe}{m\beta^2}+\frac{Xe}{m\beta}\left[\frac{2m(a+x')}{Xe}\right]^{1/2}\right)\\&-2e^{-\beta(2mx'/Xe)^{1/2}}\left(\frac{Xe}{m\beta^2}+\frac{Xe}{m\beta}\left[\frac{2mx'}{Xe}\right]^{1/2}\right)\Bigg\}\end{aligned} \tag{8}$$

where x' is the distance measured from the center of the beam, i.e., $x=a+x'$. This again tells us that I is directly proportional to the electron density. I must have a maximum value for some value of x' which can be found by differentiating Eq. (8) with respect to x' and equating to zero. On doing this, (8) gives

$$2e^{-\beta(2mx'/Xe)^{1/2}}-e^{-\beta[2m(a+x')/Xe]^{1/2}}-1=0 \tag{9}$$

This equation now gives a method for determining the average life of the excited state. Having mentioned above that the light is directly proportional to the electron current density we see that the intensity must be the result

of a single collision and hence Eqs. (7) and (8) should agree with the experimental results. Also having obtained from Curve 1 the distance the spark line has been displaced from the center of the beam we then substitute this value in Eq. (9) for x' and then determine the constant β which gives directly the mean life. The value obtained is 4×10^{-7} seconds. Thus having obtained β we can substitute it in Eqs. (7) and (8) and obtain a theoretical intensity curve which is shown in Fig. 3, by the dotted line. The agreement between this and the experimental Curve 2 is quite good.

Part II. *Double collision.* In this case we have, similar to (4) above,

$$I=A'\beta\gamma\int_{\xi=0}^{x}\int_{\eta=\xi}^{x}N^2\epsilon^{-[\gamma Nt(\xi,\eta)+\beta t(x,\eta,\xi)]}\frac{dt(\eta,\xi)}{d\eta}\,\frac{dt(x,\eta,\xi)}{dx}d\xi d\eta$$

But now $N=k\xi$ for values of $\xi\leqq a$; $N=2ka-k\xi$ for values of $\xi\geqq a$.

This expression is not easily integrated but it can be shown on substituting the numerical values that the intensity will be proportional to the square of the electron current provided γ is small. For values of γ not small the intensity will be a function of k and x for given conditions and the intensity ratio for two different currents will depend on the value of x at which the measurements are taken. In view of the above results we conclude that this type of action is not occurring.

Life of the excited state for the lines of the first spark spectrum. In this case of the narrow beam the lines due to singly charged ions did not show a displacement from the center of the beam. From Eq. (9) it can be shown that if the life of the excited ion was of the order of 10^{-8} seconds it would not exhibit a shift large enough to be measured. It is therefore concluded that its mean life must be of that magnitude.

In these calculations it has been assumed that the velocity of ions is that given to it by the external fields. No account has been taken of the fields produced by the ions themselves. The order of magnitude of the positive ion current collected by the side electrode was 1×10^{-5} amperes per cm^2. The electron current was 1×10^{-4} amperes per cm^2. The resultant charge in the beam must be positive and the disturbing fields produced is small compared to the external field of 200 volts per cm which was used in obtaining the results illustrated in Fig. 3. The good agreement between the theoretical and experimental curves indicates that the observed phenomena can be explained according to the previous assumptions.

The writer wishes to acknowledge his indebtedness to Professor W. F. G. Swann for outlining the method for calculating these intensities and to thank him for his interest in the work. The writer also desires to thank Professor James Barnes for the privilege of using the densitometer at Bryn Mawr College.

BARTOL RESEARCH FOUNDATION,
THE FRANKLIN INSTITUTE,
July 16, 1928.

IONIZING POTENTIALS AND FAR ULTRA-VIOLET LINES OF LIGHT ATOMS

By Louis A. Turner

Abstract

By an interpolation the ionizing potentials of F and F^+ are found to be 17.4 and 34.5 volts. These new values improve the regularity of the relationships of the values of $(\nu/R)^{1/2}$ corresponding to the ionizing potentials of the atoms of the first short period. The energy necessary for the removal of a $2s$ electron from each of many of the atoms and ions of these elements (L_{II} levels for an atom) is calculated by use of the $s^2p^{n-1}-sp^n$ lines.

The effect of the removal of a $2s$ electron upon the subsequent removal of a $2p$ electron is found for B, F, and Ne to be an increase of $(\nu/R)^{1/2}$ by about 0.45. This is used to get a prediction of the wave-lengths of missing $s^2p^{n-1}-sp^n$ lines of C, N, N^+, and O.

New identifications of the far ultra-violet lines of Mg are proposed and the third ionizing potential found to be 80.4 ± 1 volts. A pair of lines of F are tentatively identified as the $2s^22p^5\ {}^2P-2s2p^6\ {}^2S$ lines.

RECENT work on the measurement and analysis of the far ultra-violet spectra of many atoms and ions by Millikan and Bowen and others has made it possible to determine their ionizing potentials with great accuracy. Millikan and Bowen[1] have published a table of the ionizing potentials of the atoms and ions of the first short period of the periodic table and a graph which shows strikingly simple relationships between the square roots of these energies necessary for the removal of outer $2p$ electrons. Lines drawn through points for iso-electronic ions are nearly parallel. The purpose of the present paper is to discuss certain extensions and minor amendments of this graph, to calculate from the spectroscopic data the ionizing potentials for the removal of a $2s$ electron (L_{II} levels of the neutral atoms) and show the similar relations between them, and to discuss the results of certain extrapolations.

Ionization by Removal of a $2p$ Electron

For the atoms from Be to Ne, inclusive, and the ions of similar electronic configuration, the ordinary ionizing potentials measure the energies for the removal of one of the outer group of equivalent $2p$ electrons. These are the ones discussed by Millikan and Bowen. For the elements whose spectra in the visible and near ultra-violet regions have been extensively analyzed the measurement of the related far ultra-violet lines involving the transitions to the normal state gives accurate values of the ionizing potentials. For the others, Bowen,[2] who calculated most of these ionizing potentials, had to make highly plausible assumptions concerning the values of certain high

[1] R. A. Millikan and I. S. Bowen, Proc. Nat. Acad. Sci., **13**, 531 (1927).

[2] I. S. Bowen, Phys. Rev. **29**, 231 (1927).

terms which are connected with configurations in which the excited electron is a $3d$, presumably non-penetrating and giving a hydrogen-like term in these light atoms. Such a fixation of any one term implies certain values for all other terms, including the normal one, and therefore of the ionizing potential. One can calculate the energy in agreement with each of these ionizing potentials for the removal of the $3s$ electron from the configuration $2s^22p^{n-1}3s$. These energies which are simply the corresponding term values expressed in volts are given in Table I. The $2s^22p^{n-1}3s$ configuration is an excited one for all of these atoms and ions except Na and Mg^+ whose normal configuration is entirely analogous to this excited configuration of the others.

TABLE I *Energy for removal of a 3s electron*

Atom	Term	Energy (volts)	Reference	Ion	Term	Energy	Reference
Na	^2S	**5.116**	A	Mg^+	^2S	**14.96**	A
Ne	$^3P_1$	**4.89**	A	Na^+	$^3P_1$	14.2	H
F	$^2P_2$	4.0	B	Ne^+	$^2P_2$	**13.13**	G
O	^3S	**4.08**	C	F^+	^3S	9.6	B
N	$^4P_1$	**4.20**	D	O^+	$^4P_1$	**12.09**	F
C	$^3P_0$	**3.78**	K	N^+	$^3P_0$	**11.09**	J
B	^2S	**3.34**	I	C^+	^2S	**9.90**	E

A. Older work. See J. Franck and P. Jordan, "Anregung von Quantensprüngen durch Stösse."

B. I. S. Bowen, Phys. Rev. **29**, 231 (1927).

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D. J. J. Hopfield, Phys. Rev., **27**, 801 (1926).

E. A. Fowler, Proc. Roy. Soc. **105 A**, 299 (1924).

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The values which are printed in heavy type depend upon some sort of an analysis of series and are therefore the more accurate. References to work other than that of Bowen are to the work upon which he based his calculation of the ionizing potential of the ion concerned, or to already fairly completely analyzed spectra (Na, Mg^+, Ne O, N), or to more recent work (B, C, N^+, Ne^+, Na^+). These configurations give, in most cases, several levels. The particular one for which the energy is calculated is indicated in the table.

A study of this table leads one to suspect that the values for F and F^+ are too small. That for Ne^+ being greater than the one for O^+, one would expect the value for F to be greater than that for N. Similarly one would expect the value for F^+ to be greater than that for C^+ since the O value is surely greater than that for B. Omitting F and F^+, the ratios of the two values of iso-electronic pairs are found to be nearly constant. The Mg^+/Na, Na^+/Ne, O^+/N, N^+/C and C^+/B ratios are, respectively, 2.92, 2.90, 2.88, 2.94 and 2.96. I know of no theoretical reason for the approximate constancy of this ratio but it seems to hold well enough to serve as a basis for an interpolation to get new values for F and F^+. If we assume a ratio of 2.90 the calcu-

lated values for F and F^+ become 4.5 and 11.8 presumably accurate to 0.1 volt if one grants the validity of the method of interpolation. Bowen's values for the two ionizing potentials of F of 16.9 and 32.3 volts should be raised to 17.4 and 34.5 volts, respectively. It should be mentioned that the identifications of lines upon which his values for F and F^+ were based were the most uncertain of any and the results offered as being merely tentative.

Table II gives the ionizing potentials of the atoms and ions, the same as those of Millikan and Bowen except for the changes of the values for F and F^+, slight changes of the values for B, C, and N^+ based upon newer analyses, and with the addition of the new values for Na^+ and Ne^+. These are the

TABLE II. *Ionization by removal of a 2p electron*

Element	Ionizing Potential (Volts)	$(\nu/R)^{1/2}$	$\Delta(\nu/R)^{1/2}$
B	8.28	0.78	
			0.56
C^+	24.26	1.34	
			0.53
N^{++}	47.2	1.87	
			0.52
O^{+++}	77.0	2.39	
C	11.21	0.91	
			0.57
N^+	29.50	1.48	
			0.53
O^{++}	54.8	2.01	
N	14.49	1.03	
			0.58
O^+	35.00	1.61	
O	13.56	1.00	
			0.60
F^+	34.5	1.60	
F	17.4	1.13	
			0.61
Ne^+	40.9	1.74	
Ne	21.47	1.26	
			0.61
Na^+	47.0	1.87	

energies necessary for the removal of a $2p$ electron from an atom or ion in the state corresponding to the lowest level connected with the normal $2s^2 2p^n$ configuration, leaving the ion so formed in its normal state. From these are calculated the corresponding values of $(\nu/R)^{1/2}$ and the differences of $(\nu/R)^{1/2}$ between iso-electronic ions, which give the slopes of the lines connecting adjacent iso-electronic points. They run much more smoothly than with the unchanged values of F and F^+ as is seen by reference to Fig. 1 which gives the Moseley diagram like that of Millikan and Bowen but with the addition of the new points for Na^+ and Ne^+ and the changed ones for F and F^+.

This change of the ionizing potential of F introduces a difficulty in the interpretation of the strong 806.92 and 809.60 lines. Bowen identified them as lines arising from a transition to the normal ^2P state from a level which he called $3nx$, signifying that it was one of the levels of the $2s^22p^43d$ configuration. He assigned it a term value of 13,000 wave-number units assuming that such terms have hydrogen-like values as they have been found to have in the completely analyzed spectra of others of these light atoms. If, however, the ionizing potential is to be raised by 0.5 volts this term value becomes approximately 17,050 which is much too high for a term arising from the $2s^22p^43d$ configuration. It is, however, apparently too small to be explained as either the ^2D or ^2S term arising from the $2s^22p^43s$ configuration. It might possibly be the ^2S term of the $2s2p^2$ configuration, the two lines being analogous to the strong 462 pair of Ne^+. This possibility is discussed more fully below.

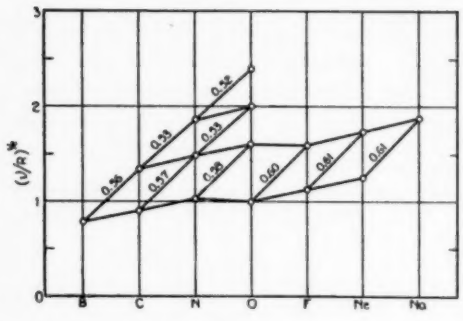


Fig. 1. Moseley diagram for removal of $2p$ electron for elements B to Na.

Ionization by Removal of a 2s Electron

Among the strongest lines in these far ultra-violet spectra are lines whose frequencies for iso-electronic sequences follow the irregular doublet law. This indicates that the total quantum number of the electron which changes must be the same in both the initial and final states. Millikan and Bowen interpret these lines as resulting from transitions in which a $2p$ electron replaces a missing $2s$ electron. That is, if $2s^22p^n$ be the normal configuration the atom or ion is somehow ionized by the removal of a $2s$ electron to give $2s2p^n$ which then emits one of the lines under consideration as a $2p$ electron jumps to replace the missing $2s$ electron giving finally $2s^22p^{n-1}$, the same as if a $2p$ electron had been removed originally. This is essentially an x-ray process of emission by the reorganization of the ion after the removal of an inner electron. Such lines will be referred to as $s^2p^{n-1}-sp^n$ lines. Their measurement and identification having been carried out all the data are now available for calculating the energy necessary to remove a $2s$ electron from each of these atoms and ions.

Take oxygen as an example. The normal configuration is $2s^22p^4$, the s group being closed, and the four p electrons giving rise to ^3P, ^1D and ^1S terms. The removal of a $2s$ electron will leave a single $2s$ electron and the $2s2p^4$ configuration of the ion will give ^4P, ^2P, ^2D and ^2S terms as does the $2s^22p^43s$ configuration of F. There will be, therefore, a whole set of ionizing potentials for the removal of the $2s$ electron corresponding to these various possible states of the ion just as, of course, there is a whole set of possible ionizing potentials for the ordinary ionization by removal of a $2p$ electron,

corresponding to the various possible states of the ion after such an ionization. It is customary to refer to the one of least energy as *the* ionizing potential and the same convention may well be adopted for ionization by removal of a 2*s* electron. With the 2*s* electron gone an electron from the $2p^4$ group may then take its place, radiating an $s^2p^{n-1}-sp^n$ line of the *spark* spectrum and leaving the ion in one of the states resulting from the $2s^22p^3$ configuration, viz., ^4S, ^2D, ^2P. Thus one can compute the energy for the removal of an electron to leave the ion in the $2s2p^4\ ^4P_3$ level by adding to the ordinary ionizing potential ($2s^22p^4\ ^3P_0 \rightarrow 2s^22p^3\ ^4S$) the energy corresponding to the emission of the $2s^22p^3\ ^4S-2s2p^4\ ^4P_3$ line (834.46 A.U.). Similarly one computes the energy for removal of a 2*s* electron from an already once ionized atom (one 2*p* gone) by adding to the ordinary second ionizing potential the energy corresponding to the appropriate $s^2p^{n-1}-sp^n$ line of the *second* spark spectrum, and so forth. It seems possible that the great strength of these lines as compared with others of the same spectrum may result because they can be produced by the act of removal of a single 2*s* electron, while the others depend upon the removal of one electron and the simultaneous or subsequent excitation of another one. It would be of interest to investigate the excitation of these ions by single impact of electrons of known speeds to see whether this type of internal ionization is one of high probability. It may be, however, that the great intensity of these lines is simply a result of the circumstance that the energy necessary for their excitation is in general less than that necessary for excitation of other spark lines.

TABLE III. *Energy for removal of a 3s electron.*

$2s^22p^n$ Atom or Ion	$2s^22p^{n-1}$ Term	$s^2p^{n-1}-sp^n$ Line	$2s2p^n$ Term (Final state of ion with 2*s* electron gone)	Energy	$(\nu/R)^{1/2}$	$\Delta(\nu/R)^{1/2}$
B	^1S	3452	^3P	11.9	0.94	0.54
C^+	^1S	2297	^3P	29.6	1.48	
C	^3P	1334	^3D	20.5	1.23	0.55
N^+	^3P	990	^3D	43.1	1.78	0.50
O^{++}	^3P	790	^3D	70.4	2.28	
N	^3P	1084	^3D	25.9	1.38	0.54
O^+	^3P	834	^3D	49.8	1.92	
O	^4S	832	^4P	28.4	1.45	0.54
F^+	^4S	657	^4P	53.3	1.99	
F	^3P	605	^3P	37.7	1.67	
Ne	^2P	462	^2S	48.2	1.89	

Table III gives the results of these calculations for those atoms and ions for which there is sufficient data. These are the L_{II} x-ray levels for the neutral atoms. In a few cases not all of the theoretically predicted $s^2p^{n-1}-sp^n$ lines have been identified so that the calculated ionizing potential is for a somewhat excited level of the sp^n configuration and not for the lowest one. In these cases the term designation is put in bold face in the table. These points are plotted in Fig. 2. That lines of nearly the same slope as those of the previous diagram can be drawn through the adjacent iso-electronic points is of course not surprising since that is what is implied by the fact that the irregular doublet law is applicable. The slopes are, however, definitely less for the $2s$ electrons than for the $2p$ electrons and stay constant rather than increasing with increasing atomic number.

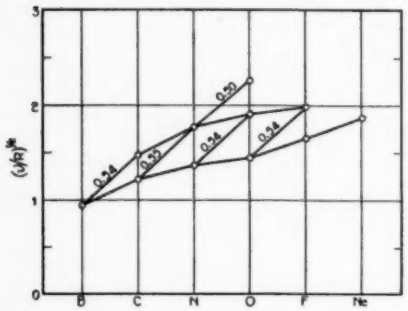


Fig. 2. Moseley diagram for the removal of the $2s$ electron for the elements B to Ne.

If we assume that the same value of 0.54 will be found for the Ne^+-F difference, and the Na^+-Ne difference, these ionizing potentials for Ne^+ and Na^+ are calculated to be 66.0 and 80.0 volts respectively. The $2s^22p^4-2s2p^5$ transition in Ne^{++} thus involves an energy difference of $66.0-40.9=25.1$ volts and would give rise to a group of lines in the neighborhood of 492 A.U. This is on the side of longer wave-lengths of the corresponding sort of lines of Ne^+ (462 A.U.). Such a group in this relative position has been found in the spectrum of argon by Dorgelo and Abbink.[3] The $2s^22p^5-2s^2p^6$ transition of Na^{++} involves an energy difference of $80.0-47.0=33.0$ volts and should thus give another pair of lines, not yet found, at 374 A.U. The hypothetical $2s^22p^53s^3P$, $^1P-2s2p^63s^3S$, ^1S lines would appear at nearly the same wave-length since the presence of the outer $3s$ electron would probably not affect the energy difference greatly.

Screening Effect of s Electrons

A certain amount of energy is required in order to remove both a $2p$ electron and a $2s$ electron and must be the same regardless of the order in which they are removed if the same final state is reached. The sum of the energy for removal of a $2p$ electron (ordinary I.P.) and the energy for removal of a $2s$ electron from the ion thus formed (Table III) must equal the sum of the energy of removal of a $2s$ electron from the neutral atom and the energy of subsequent removal of a $2p$ electron. The first three quantities being known the fourth can be calculated. Unfortunately, significant results can be obtained for only B, F and Ne because either one or the other of the lowest sp^n terms involved in the calculation is unknown for C, N, and O. Table IV gives the results for the three elements.

[3] Dorgelo and Abbink, Zeits. f. Physik. **41**, 753, (1927).

TABLE IV. *Energy for removal of a 2p electron from an ion produced by previous removal of a 2s electron.*

Atom	Energy	$(\nu/R)^{1/2}$	$(\nu/R)^{1/2}$ for ordinary I. P.	$\Delta(\nu/R)^{1/2}$
B	20.6	1.24	0.78	0.46
F	33.0	1.56	1.13	0.43
Ne	39.3	1.71	1.26	0.45

Apparently the previous removal of a 2*s* electron raises the energy for subsequent removal of a 2*p* electron in a way such that the $(\nu/R)^{1/2}$ value ncreases by about 0.45. If this relationship be assumed to hold approximately for the other atoms one can calculate this energy for C, N, and O and then work backwards to get an estimate of the wave-lengths of the missing $s^2p^{n-1}-sp^n$ lines. For instance, take C. $(\nu/R)^{1/2}$ for the ordinary ionizing potential is 0.91. Adding 0.45 gives 1.36, corresponding to an energy of 25.0 volts for the removal of a 2*p* electron after the removal of a 2*s*. The sum of the ordinary ionizing potential and the 2*s* ionizing potential of C^+ is 40.9 volts. Subtracting 25.0 thus gives 15.9 volts as the energy for removal of a 2*s* electron from the un-ionized C atom to give the $2s2p^2\ {}^4P$ term. The ordinary I.P. being 11.3 volts the difference of 4.6 volts is the amount of energy radiated in the $s^2p^{n-1}-sp^n$ lines. These lines will be the $2s^22p\ {}^2P - 2s2p^2\ {}^4P$ lines of the CII spectrum and thus be a group of 5 lines involving the doublet difference of 63.8 units of the low ^2P of C^+ twice and be located near 2700 A.U. Since the energy value of 4.6 volts may well be in error by 0.5 volt these lines should be looked for in the region from 2400 to 3000 A.U.

Similarly, the energy for removal of a 2*p* electron from an oxygen atom from which has already been removed one 2*s* electron is 28.4 volts. The energy for removal of the 2*s* electron in the first place being also 28.4 volts, the total for the double ionization is 56.8 volts. Subtracting the ordinary ionizing potential of O of 13.6 volts gives a value of 43.2 volts for the removal of a 2*s* electron from the ordinary O^+ ion. The ordinary second ionizing potential is 35.0 volts, the difference of 8.2 volts being the amount of energy to be radiated in the $2s^22p^2\ {}^3P - 2s2p^3\ {}^5S$ lines of the O III spectrum at about 1500 A.U. (A pair having the frequency difference equal to that between the $^3P_1$ and $^3P_2$ levels.)

It is not possible to proceed in the same manner to make the corresponding calculations for N since neither the lowest term of N^+ $2s2p^3(^5S)$ nor that of N^{++} $2s2p^2(^4P)$ is known. One can, however, take the value of 43.2 volts for O^+, just found, corresponding to a value of $(\nu/R)^{1/2}$ of 1.79, subtract from it the value of 0.54 of Table III to get 1.25 corresponding to 21.1 volts for N, the energy to remove a 2*s* electron from N leaving the ion in the $2s2p^3(^5S)$ state. The ordinary ionizing potential is 14.5 volts so the difference of 6.5 volts would be found in the $2s^22p^2\ {}^3P - 2s2p^3\ {}^5S$ lines of N^+ at about 1900 A.U. Similarly, using the value for the removal of a 2*s* electron from a C atom found above (15.9 volts) the corresponding energy of removal of a 2*s* electron from an ordinary N^+ ion to get the lowest term, $2s2p^2\ {}^4P$, is found to be 36.0 volts. The $2s^22p\ {}^2P - 2s2p^2\ {}^4P$ lines of N^{++} should be found at

about 1930 A.U. The two new values for N just found are checked as follows. The energies for removal first of a $2p$ and then of a $2s$ electron are 14.5 and 36.0 volts giving a total of 50.5 volts. Removing them in the opposite order the energies are 21.1 and 29.6 volts giving a sum of 50.7 volts which gives a rather surprisingly good agreement in view of the number of extrapolations involved in the calculations. (The value of 29.6 volts for removal of a $2p$ electron after previous removal of a $2s$ was calculated by use of the $(\nu/R)^{1/2}$ difference of 0.45 as above.)

I have not been able to find published data with which to test the predictions here made concerning the location of the missing $sp^n - s^2p^{n-1}$ lines. They are all predicted to be at considerably greater wave-lengths than the other such lines already found in these spectra of the same ions.

Lines of Mg in the Far Ultra-violet

The value of $(\nu/R)^{1/2}$ corresponding to the ionizing potential of Na^+ of 47.0 volts is 1.87, that for Ne is 1.26 (Table I), giving a difference of 0.61. If we assume that the difference between Mg^{++} and Na^+ is also 0.61 the ionizing potential of Mg^{++} is calculated to be 83.1 volts. If, however, we take for the difference between Mg^{++} and Na^+ the difference of 0.53 found between N^{++} and C^+, and O^{++} and N^+, the value for Mg^{++} comes out 77.8 volts. An intermediate value seems more probable. Taking 0.57 for the difference one gets 80.4 volts. This is the energy for the removal of a $2p$ electron from the $2s^22p^6$ configuration of Mg^{++}.

The energy for the removal of the $3s$ electron from the $2s^22p^53s$ configuration of Mg^{++} can be calculated on the assumption that its ratio to the corresponding energy for the same configuration of Ne is equal to the ratio of the energies for removal of the $3s$ electrons of Al^{++} and Na (Ionizing potentials, see Franck and Jordan, loc. cit.)

$$Mg^{++}\ 2s^22p^5(3s) \rightarrow 2s^22p^5$$

$$4.89\ \frac{28.3}{5.116} = 27.0 \text{ volts.}$$

The difference between these two energies, $80.4 - 27.0 = 53.4$ volts is the energy which is emitted in the $2s^22p^6\ {}^1S - 2s^22p^53s\ {}^3P,\ {}^1P$ lines, analogous to the two resonance lines of Ne. The energy of 53.4 volts corresponds to a wave-length of 231 A.U. Using values of the ionizing potential of 83.1 or 77.8 volts instead of 80.4 volts this wave-length comes out to be 220 or 244 A.U., respectively. The possible $2s^22p^63s\ {}^2S - 2s^22p^53s^2\ {}^2P$ transition would also give a pair of lines at nearly the same wave-length since the presence of one more outer $3s$ electron would presumably not affect the energy difference to any great extent.

Millikan[4] found three strong lines in the far ultra-violet spectrum of Mg.

Intensity	λ	Volts
2	231.4	53.4
5	320.9	38.5
4	323.2	38.2

[4] R. A. Millikan, Phys. Rev. **23**, 1, (1924).

It appears that the 231.4 line is emitted when one of these two transitions takes place, and not the other pair of lines as has been suggested.[4] There should be another line accompanying it, however, and presumably resolvably separated from it. Of the two possible transitions which might give rise to this line the $2s^22p^6-2s^22p^5\ 3s$ one seems to be the more probable since the pair of lines which it gives are $^1S-{}^1P$ and $^1S-{}^3P$ lines, the former being much stronger because of the relative weakness of intercombination lines in light atoms. The $2s^22p^6\ 3s-2s^22p^5\ 3s^2$ transition would give a $^2S-{}^2P$ doublet, probably of more nearly equal intensity. These latter lines would of course be the L_α lines. If this identification of the 231.4 line be accepted the third ionizing potential of Mg is thus found to be 80.4 volts, since the wave-length computed on the assumption of that value agrees with the one actually found. This value is in error by the amount of the error in the estimation of the energy necessary to remove the $3s$ electron from the $2s^22p^53s$ configuration of Mg^{++}, perhaps 1 volt.

The 320.9 and 323.2 lines can, however, be identified as lines emitted during the transition of an electron from a $2p$ to a $2s$ orbit. Table III shows that the $(\nu/R)^{1/2}$ difference between O^{++} and C for the removal of a $2s$ electron is 1.05. If we assume that the same difference will be found between Mg^{++} and Ne, the $(\nu/R)^{1/2}$ value for Mg^{++} is $1.89+1.05=2.94$ corresponding to an energy of 117.0 volts. The energy for the removal of a $2p$ electron being 80.4 volts, the energy difference which would be emitted as the $2s^22p^5-2s2p^6$ lines is $117.0-80.4=36.6$ volts corresponding to a wave-length of 338 A.U. This agrees well enough with the wave-lengths of the lines found by Millikan, in view of the extrapolation involved. The possible transitions which would give lines of about the same wave-length are as follows:

$2s^22p^5-2s2p^6$	$^2P-{}^2S$	two lines
$2s^22p^53s-2s2p^63s$	$^3P,{}^1P-{}^3S,{}^1S$	six lines (four strong)
$2s^22p^53s^2-2s2p^63s^2$	$^2P-{}^2S$	two lines

There does not seem to be any way to decide between the first and the third possibilities. The third would result from the removal of but one electron from the normal Mg atoms. It should be possible to excite lines of approximately this wave-length by bombarding a target of solid Mg since these are essentially x-ray lines. If the identification of these lines be assumed the energy for the removal of the $2s$ electron can be calculated to be $80.4+38.2=118.6$ volts, with considerable error because of the uncertainty as to which of the two possible transitions give rise to the lines observed.

The Fluorine Lines

As mentioned above, the change of the ionizing potential of F involves a difficulty in the interpretation of the 806.92 and 809.60 lines which arise from the combination of some excited term with the normal ^2P term. The excited term may possibly be the $2s2p^6\ ^2S$ term. If the line of Fig. 1 through the points for Ne and Na^+ be extrapolated backward it gives a value of 0.65 for F^- which gives an upper limit of 5.7 volts for the electron affinity of F. This is thought to be an upper limit because of the tendency shown

for the differences of $(\nu/R)^{1/2}$ to increase with decreasing net charges of the two ions concerned. If the proper difference be 0.65 one gets a value of 5.0 volts for this electron affinity. The 806.92 line corresponds to an energy of 15.3 volts so that if these lines are the $2s^22p^5-2s2p^6$ lines the energy of the $2s2p^6$ level referred to the $2s^22p^6$ F^- ion must be $5.0+15.3=20.3$ volts. This gives a $(\nu/R)^{1/2}$ value of 1.23. That for Ne being 1.89, the difference is 0.66 which seems like too great an increase over the difference of 0.54 found between the $(\nu/R)^{1/2}$ values for the various neutral atoms and singly positively charged ions. If this difference were to be less the energy of the $2s2p^6$ term would be greater and the $2s^22p^5-2s2p^6$ lines lie at shorter wave-lengths. Since they would presumably be strong, in the region investigated by Millikan and Bowen, and with the frequency difference characteristic of the normal ^2P term the fact that they have not been reported probably indicates that they are not there and gives support to the present identification of the 806.92 and 809.60 lines.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
July, 1928.

Note added with proof Sept. 20, 1928.—

I am much indebted to Dr. I. S. Bowen for a letter in which he has made valuable comments upon several of the points discussed in this paper and has referred me to several newer analyses of spectra which I had overlooked. The newer data, which involved changes of several ionizing potentials by a few hundredths of a volt, have been incorporated into the above tables. Bowen states that the old identifications[5] of the 3452 line of B^+ and the 2297 line of C^{++} as $^1S-{}^3P_1$ lines are most certainly wrong inasmuch as these are very strong lines and the intercombination lines in the spectra of other light elements are now known to be very weak, and that the true $^1S-{}^3P_1$ lines not yet found probably lie at longer wave-lengths. The energy values of Table III for B and C^+ are thus probably too great and that of Table IV for B somewhat too small. Likewise the predicted wave-lengths for the missing lines of the C II spectrum and the N III spectrum are too small. Bowen suggests that the missing $s^2p^{n-1}-sp^n$ lines will be very difficult to find because they too are intercombination lines and will presumably be very weak. Those of the C II spectrum do not appear in the extensive tables of the recent paper of Fowler and Selwyn[6].

He also called my attention to the fact that Dingle[7] has already made the same suggestion concerning the interpretation of the 806–809 pair of F. In that paper Dingle computes a value for the ionizing potential of F of 18.6 volts by use of the Rydberg formula with two ^2P terms, one of these being the lowest term, but states that the value is probably too high.

[5] I. S. Bowen and R. A. Millikan, Phys. Rev. **26**, 310 (1925).
[6] A. Fowler and E. W. H. Selwyn, Proc. Soc. **120A**, 312 (1928).
[7] H. Dingle, Proc. Roy. Soc. **117A**, 416 (1928).

ON THE SPECTRA OF DOUBLY IONIZED ARSENIC ANTIMONY AND BISMUTH (As III, Sb III, Bi III)

By R. J. Lang

Abstract

The spectra of the elements As III, Sb III and Bi III have been partially analyzed by the use of the irregular doublet law and the Moseley law and the published data for the two preceding elements of each iso-electronic sequence. In As III and Bi III the important terms from the configurations ns^2np, ns^2nd, $ns^2(n+1)s$ have been located and with the exception of the quartet P terms, those from the $nsnp^2$ configuration. (n is equal to 4 for As III, 5 for Sb III and 6 for Bi III.) In As III alone the ^2P term of the np^3 configuration was found. The terms of Sb III located consist of some of those for the first three configurations only.

THE spectra of arsenic, antimony and bismuth should be very similar and since those of the two preceding elements in each iso-electric sequence have been partially analyzed it is possible to predict the doublet separations of the chief terms and the positions in the spectrum of some of the main line groups. References to the work of other investigators which has been used in this report are as follows: Ga I,[1] In I,[1] Tl I,[1] Ge II,[2] Sn II,[3] Pb II.[4]

Most of the wave-length measurements recorded were made on a two-meter grating mounted in a vacuum spectrograph using the hot spark between metallic electrodes as source, but a few of the longer wave-lengths are taken from Kayser's Handbuch der Spektroskopie. The measurements for wave-lengths greater than 2000A are given in I.A. in air and for those less than this value in I.A. in vacuo.

The most important configurations of the iso-electronic sequences and the important terms arising from them in order of decreasing stability are as follows:

Configuration	Term	Configuration	Terms
n^*s^2np	^2P	$ns\ np^2$	$^4P\ ^2D\ ^2P\ ^2S$
ns^2nd	^2D	np^3	$^2P\ ^2D\ ^4S$
$ns^2(n+1)s$	^2S		

The first three rows on the left give the terms from the normal configuration (ns^2) of the next higher ion, the first row on the right gives the terms from the ($nsnp$) configuration of the ion and in the second row are recorded those terms to be expected from (np^2).

Tables I, II, and III give the term values and classified lines in As III, Sb III and Bi III respectively. The terms in each case are divided into

[1] Fowler, "Report on Series in Line Spectra."

[2] Lang, Proc. Nat. Acad. Sci. **14**, 32 (Jan., 1928).

[3] Green and Loring, Phys. Rev. **30**, 5 (Nov., 1927).

[4] Gieseler, Zeits. f. Physik **42**, 4 (1927).

* n has the value 4 for the first sequence, 5 for the second and 6 for the third.

odd and even and the configuration from which each arises is recorded. To save space, however, these configurations are not repeated in the designation of the lines in the first column of these tables. In order that it might be

TABLE I. *Term values and classified lines in the spectrum of As III.*

Designation	λ(I A.)	I	ν	Δν
$bS-5P_1$	4226.87	6	23652	722
$bS-5P_2$	4101.49	6	24374	
$5S-5P_1$	4037.17	15	24763	723
$5S-5P_2$	3922.61	20	25486	
$5P_2-6S$	3255.69	8	30706	723
$5P_1-6S$	3180.78	5	31429	
$5P_2-5D_2$	2989.54	2	33441	84
$5P_2-5D_3$	2982.00	15	33525	722
$5P_1-5D_2$	2926.32	10	34163	
bP_2-cP_2	2151.58	4	46461	163
bP_2-cP_1	2144.13	4	46624	2224
bP_1-cP_2	2053.31	1	48685	
bP_1-cP_1	—	—	(48848)	
bD_2-5P_2	2133.89	1	46870	321
bD_3-5P_2	2147.59	5	46549	722
bD_2-5P_1	2166.28	2	46148	
bD_2-cP_2	1274.28	8	78476	327
bD_3-cP_2	1268.97	5	78803	162
bD_2-cP_1	1266.39	30	78965	
$4P_2-bD_2$	1214.00	3	82372	321
$4P_2-bD_3$	1209.28	15	82693	2941
$4P_1-bD_2$	1172.15	12	85313	
$4P_2-5S$	963.75	20	103760	2941
$4P_1-5S$	937.20	20	106701	
$4P_2-bS$	953.57	20	104869	2945
$4P_1-bS$	927.52	20	107814	
$4P_2-bP_1$	888.98	20	112488	
$4P_2-bP_2$	871.73	25	114714	2948
$4P_1-bP_1$	866.28	15	115436	2946
$4P_1-bP_2$	849.91	15	117660	
$4P_2-4D_2$	849.34	1	117739	484
$4P_2-4D_3$	845.86	2	118223	2939
$4P_1-4D_2$	828.65	2	120678	
$4P_2-5D_2$	614.73	0	162673	85
$4P_2-5D_3$	614.41	3	162758	2942
$4P_1-5D_2$	603.81	3	165615	

Odd Terms

Configuration	Term Values	
$4s^24p$	$4P_1$	0
	$4P_2$	2945
$4s^25p$	$5P_1$	131465
	$5P_2$	132185
$4p^3$	cP_1	164284
	cP_2	164121

Even Terms

Configuration	Term Values	
$4s^25s$	$5S$	106700
$4s^26s$	$6S$	162893
$4s^24d$	$4D_2$	120684
	$4D_3$	121168
$4s^25d$	$5D_2$	165631
	$5D_3$	165712
$4s\ 4p^2$	bD_2	85316
	bD_3	85638
$4s\ 4p^2$	bP_1	115435
	bP_2	117659
$4s\ 4p^2$	bS	107814

clear just which term is meant in any given case it was decided to use the total quantum number of the added electron for the terms arising from (ns^2) of the higher ion, while in the case of terms from the state $(nsnp)$ of the ion the letter b is used and for the terms from (p^2) the letter c is used.

TABLE II. *Term values and classified lines in the spectrum of Sb III.*

Designation	λ(I.A.)	I	ν	Δν
$6S-6P_2$	4352.25	6u	22970	1668
$6S-6P_1$	4693.09	4u	21302	
$6P_2-7S$	3739.95	4u	26730.7	1669.3
$6P_1-7S$	3520.11	1u	28400.0	
$6P_2-6D_2$	3534.17	1	28287	237
$6P_2-6D_3$	3504.79	15	28524	1670
$6P_1-6D_2$	3337.10	12	29957	

Odd Terms		
Configuration	Term Value	
$5s^26p$	$6P_1$	21302
	$6P_2$	22970
Even Terms		
Configuration	Term Value	
$5s^26s$	$6S$	0
$5s^27s$	$7S$	49702
$5s^26d$	$6D_2$	51259
	$6D_3$	51496

TABLE III. *Term values and classified lines in the spectrum of Bi III.*

Designation	λ(I.A.)	I	ν	Δν
$7P_2-7D_2$	3708.51	6	26957	710
$7P_2-7D_3$	3613.41	35	27667	5133
$7P_1-7D_2$	3115.20	20	32091	
$7S-7P_2$	3695.70	50	27051.9	5133.7
$7S-7P_1$	4561.33	40	21918.2	
$6P_2-7S$	1423.47	20	70251	20373
$6P_1-7S$	1103.46	15	90624	
$6P_2-6D_2$	1350.16	15	74065	1859
$6P_2-6D_3$	1317.12	30	75924	20374
$6P_1-6D_2$	1058.88	20	94439	
$6P_2-bD_2$	1207.08	3	82845	1295
$6P_2-bD_3$	1188.50	10	84140	20373
$6P_1-bD_2$	968.82	10	103218	
$6P_2-bS$	989.87	12	101023	20373
$6P_1-bS$	823.75	10	121396	

Odd Terms		
Configuration	Term Value	
$6s^26p$	$6P_1$	0
	$6P_2$	20373
$6s^27p$	$7P_1$	112542
	$7P_2$	117676
Even Terms		
Configuration	Term Values	
$6s^27s$	$7S$	90624
$6s^26d$	$6D_2$	94438
	$6D_3$	96296
$6s^27d$	$7D_2$	144634
	$7D_3$	145344
$6s\,6p^2$	bD_2	103218
	bD_3	104513
$6s\,6p^2$	bS	121396

All the terms found are doublets; the doublet notation has been omitted for the sake of simplicity.

The results of the application of the irregular doublet law to the wave-number of the strongest lines in those multiplets which arise from inter-combinations of terms, the valence electrons for which have the same total quantum numbers, are shown in Table IV. It will be noted that for the

TABLE IV. *Position of corresponding lines by the irregular doublet law*

Line	Spectrum	ν	$\Delta\nu$	Line	Spectrum	ν	$\Delta\nu$
$4P_2-4D_3$	Ga I	33961	45281	$6P_2-6D_3$	Tl I	28407	26505
	Ge II	79242	38981		Pb II	54912	21012
	As III	118223			Bi III	75924	
$5P_2-5D_3$	Ga I	7749	13015	$7P_2-7D_3$	Tl I	6888	8348
	Ge II	20764	12761		Pb II	15236	12431
	As III	32525			Bi III	27667	
$5S-5P_2$	Ga I	8373	8590	$7S-7P_2$	Tl I	8683	9541
	Ge II	16963	8523		Pb II	18224	8828
	As III	25486			Bi III	27052	
$5P_2-5D_3$	In I	30703	37090				
	Sn II	67793					
	Sb III	—	—				
$6P_2-6D_3$	In I	6900	11069				
	Sn II	17969	10555				
	Sb III	28524					
$6S-6P_2$	In I	7775	7717				
	Sn II	15492	7478				
	Sb III	22970					

TABLE V. *Screening constants and differences by Sommerfeld formula.*

Term	Spectrum	$\Delta\nu$	σ_2	Δ	Term	Spectrum	$\Delta\nu$	σ_2	Δ
$4P$	Ga I	826	19.40	1.44	$6P$	Tl I	7793	53.43	3.40
	Ge II	1768	17.96	0.90		Pb II	14070	50.03	3.08
	As III	2943	17.06			Bi III	20373	47.95	
$5P$	Ga I	108	22.76	1.90	$7P$	Tl I	1001	62.47	5.46
	Ge II	360	20.86	1.11		Pb II	2813	58.01	3.89
	As III	722	19.75			Bi III	5134	54.12	
$4D$	Ga I	6	26.54	4.91	$6D$	Tl I	82.0	62.95	—
	Ge II	176	21.63	1.59		Pb II	—	—	
	As III	484	20.04			Bi III	1859	57.80	—
$5D$	Ga I	9	25.17	1.74	$7D$	Tl I	37.5	71.48	7.91
	Ge II	42	23.43	0.66		Pb II	29.9	63.97	3.32
	As III	85	22.77			Bi III	712	60.65	
$5P$	In I	2212	31.45	2.12					
	Sn II	4253	29.33	(1.70)					
	Sb III	(6960)	(27.62)						
$6P$	In I	292	36.86	2.86					
	Sn II	884	34.00	1.75					
	Sb III	1668	32.25						
$5D$	In I	23.5	36.66	3.63					
	Sn II	644	33.03	(4.00)					
	Sb III	(1815)	(29.00)						
$6D$	In I	50	40.05	2.52					
	Sn II	109	37.53	1.77					
	Sb III	237	35.86						

$nS-nP$ lines the doublet law holds very accurately in all the three sequences but in the case of the $nP-nD$ lines the differences Δ are quite irregular in the case of the lower quantum numbers (i.e., $4P_2-4D_3$ in the first sequence) while for the higher quantum numbers the results are quite uniform with the exception of the last sequence. As is stated below in connection with the screening constants it appears that the lines of the $6P-6D$ multiplet in Pb II may have been wrongly chosen. It should be stated here that the same failure of the irregular doublet law occurs for the $3P_2-3D_3$ lines in the sequence Al I, Si II, Pb III. That the failure is connected with the D terms may easily be seen by plotting $(\nu/R)^{1/2}$ against atomic number for these terms.

Table V gives a record of the screening constants for the doublet terms from the (ns^2) ion as calculated by Sommerfeld's formula

$$\Delta\nu = R\alpha^2(Z-\sigma_2)^4/n^3l(l+1)$$

The Calculation of Term Values

The term values in this paper have been calculated by making the value of the lowest term for each element zero. This method was finally adopted because it was found impossible to arrive at any absolute value for the terms which was not open to serious objection.

Table VI.

	Terms	Diff.	Term Value	Relative Term Value	Value of Lowest Term ($4P_1$)
	$5S$				
		12797	$5S$ 24000	24788	48790
	$6S$				
	$4P_1$				
Ga I		40376	$4P$ 49400	0	49400
	$6P_1$				
		3068	$6P$ 8050	40375	48425
	$7P_1$				
	$4D_2$				
		6021	$4D$ 13370	34782	48150
	$5D_2$				
	$5S$				
		32378	$5S$ 67020	62402	129420
	$6S$				
	$4P_1$				
Ge II		79005	$4P$ 134760	0	134760
	$5P_1$				
	$4D_2$				
		19254	$4D$ 45120	80834	125950
	$5D_2$				
	$5S$				
		56193	$5S$ 123642	106700	230340
	$6S$				
	$4P_1$				
As III		131465	$4P$ 238275	0	238275
	$5P_1$				
	$4D_2$				
		44947	$4D$ 104382	120684	225070
	$5D_2$				

The usual method of arriving at absolute term values is by applying a Rydberg or Ritz formula to the wave-numbers of several measured lines which form a series converging to one limit. This method is well known to be very exact if a sufficient number of lines of one series can be measured but in these spectra, as in nearly all spectra of higher order, not more than two lines of any one series are known. To show that in such a case it is useless to attempt to calculate absolute term values with accuracy I have taken as an example these spectra of Ga I, Ge II and As III. In Table VI, column two gives the differences between the two terms of the same sequence, which of course is independent of any chosen values for these terms, column three gives the value of the lower of the two terms derived from these differences by the use of a simple Rydberg table, and column four shows the relative values of the terms based upon the lowest term given zero value. In the last column of the table are recorded the absolute values for the lowest term calculated by assuming the Rydberg formula to hold, first for the two S terms, then for the two P terms and lastly for the two D terms. In the case of Ga I the second P term is unknown and here the first and third P terms and also the third and fourth are used.

Table VI makes it clearly evident that the values of the lowest term ($4P_1$) arrived at by this method differ very largely depending upon whether the S, P or D terms are used in the calculation. In Ga I the $6P$ and $7P$ terms are known and from these we can arrive at a value for $4P_1$ which is probably nearest to the correct value. When this is done we see that in Ga I the first P terms give a value which is much too high and also the first two S terms give too large a value while the first two D terms give probably a somewhat low value but one which is likely to be nearer the correct value. We may perhaps conclude that the most probable value for the lowest term lies between those given by the first two S terms and the first two D terms and somewhat nearer the latter.

In Table VII the most probable values for the lowest terms of the three elements of the iso-electronic sequence are given as arrived at in this way together with an estimation of the error in each and a value for the ionization

TABLE VII. *Most probable values of lowest terms and ionization potentials.*

Spectrum	Lowest term value (cm^{-1})	Ionization potential, (volts)
Ga I	48350 ± 50	5.97 ± 0.07
Ge II	127000 ± 500	15.6 ± 0.1
As III	226500 ± 1500	28.0 ± 0.2
Bi III	210000 ± 2000	25.9 ± 0.3

potential in volts. In the table will also be found an estimate of the lowest term P_1 of Bi III by means of the same method but since the $5P$ term of Sb III is still unknown no estimate has been made here but $6S$ has been made equal to zero.

Another method which has been suggested for arriving at the approximate values for the terms when few terms are known is to make the Rydberg denominators for the first S terms in an iso-electronic sequence increase by equal amounts. This method when applied to the case in hand gives about the same values for the lowest terms as were arrived at by the method outlined above. Here one must, however, assume that the term values for at least one element in the sequence are known with sufficient accuracy so that usually one cannot arrive by this method at very accurate values for the terms. Even in cases where several terms of the same series are known with fair accuracy as is the case in Ga I still a sequence of S terms gives a value considerably larger than a sequence of D terms.

A brief discussion of each of the spectra investigated will now be given.

Spectrum of As III

This spectrum seems quite regular as shown in Tables IV, V and VI with the possible exception of the nD terms. It will be found that this irregularity is a prominent feature of all of the D terms in all three sequences. It is to be expected also that the lines of this multiplet would appear with much more intensity than those recorded in Table I.

The cP terms are doubtful and in connection with the combination of these terms with bD and bP a peculiar situation was found which may be worth recording. Besides the intercombination of cP with each of these two terms bD and bP which have been recorded in Table I, three lines were found which agree within experimental error with the values expected for an intercombination between the bD and bP terms themselves. It will be seen that not only are the values rather accurate but the intensity rules are obeyed as well.

	λ	I	ν (obs)	ν (cal)
bD_2-bP_1	3319.25	(1)	30119	30119
bD_3-bP_2	3122.06	(4)	32020	32021
bD_2-bP_2	3091.18	(3)	32340	32343

The wave-lengths were taken from Kayser's Handbuch der Spektroskopie, Vol. V, and occur in the spectrum from a Geissler tube in which it appears the spectral lines of these doubly-ionized atoms frequently occur. The occurrence of these lines with wave-lengths so accurately of the predicted value may be accidental or it may mean that one of these terms should be really an odd term and that then one of the combinations with cP is unreal.

The author is greatly indebted to Dr. R. A. Sawyer for his kindness in putting the wave-length measurements of arsenic made on the vacuum spectrograph at the University of Michigan at his disposal and also for pointing out to him the significance of the strong doublet at λ953A.

Spectrum of Sb III

Two pairs of lines which evidently belong to this spectrum have been already given,[5] the less refrangible pair of which has been classified here as

[5] Nayaran and Rao, Nature, **120**, (July, 1927).

$6S-6P$ while the other falls at 4590 and 4265A. Several further pairs having this $6P$ separation have now been located including the other two listed in Table II. One of those not yet classified lies in the far infra-red[6] at 12118.9 and 10079.9A and several pairs were found in the far ultra-violet. Professor Green has very kindly taken the Zeeman pattern of the lines of the three groups of Table II and finds qualitative agreement with the classification there given except for the first group which does not seem to show quite the characteristics of a Principal pair. The same, however, may be said for the other pair at 4590 and 4265A but it would seem that these constitute about the only choice for this Principal doublet and so the pair shown in Table II has been tentatively assigned to $6S-6P$ until further information can be obtained.

The $5P$ terms of this spectrum could not be located with any degree of certainty. It was found that a value of $\Delta\nu=8100$, approximately, occurs quite frequently and it is easy to build up a plausible scheme on this basis but such a value seems much too large for the $5P$ separation as compared with In I and Sn II. Until this doublet term can be located it is not possible to proceed to the terms of the (sp^2) configuration. It may be stated that in the spectrum of the hot spark between 600 and 1200A there are some sixty lines with intensities ranging from (10) to (50) and it would seem certain that before very much progress can be made in the analysis of these complex spectra some means must be devised which will separate the lines in the extreme ultra-violet into classes corresponding more or less closely to the various stages of ionization of the atom. Such a method will of course need to be adapted to elements which exist normally in the solid state.

Spectrum of Bi III

This spectrum probably cannot be classified in a completely satisfactory manner until certain further information is available concerning the spectrum of Pb II. The reality of the two levels classified as $6D_2$ and $6D_3$ in Pb II appears to be well established but it would be indeed surprising to find in this one-electron spectrum an inverted doublet with a separation of 776 cm^{-1}. The two configurations $(6s6p^2)$ and $(6s^26d)$ are expected to give rise altogether to four levels with $j=2$ lying in the same neighborhood. Three of these have been found; it appears quite possible that the missing one is $6D_2$.

On the other hand it is quite possible on the basis of separations and intensity relations alone to find a possible multiplet in Bi III which could arise from inverted D terms simply by substituting the line 1394.05(20)71733 for the line 1317.12(30)75924 in the multiplet given in Table III.

In regard to $7P-7D$ it seems probable that the faint multiplet in Pb II has been classified incorrectly since the $7D$ term so obtained does not give a $6P-7D$ multiplet in the author's table of wave-lengths of the ultra-violet. There is a group of lines in the spectrum of Pb which may possibly be $6P-7D$ as follows:

[6] Randall, Astrophys. J. **34**, (July, 1911).

λ	I	ν
1279.44	15	78159
1274.56	10	78458
1080.84	2	92521

Of course this group is open to the same criticism which was made of $6P-6D$ above.

In conclusion the author wishes to convey to Dr. Goudsmit and to Dr. Mack of the University of Michigan his sincere thanks for very helpful criticisms in connection with the writing of this report and to express to the Research Council of Canada his appreciation of a grant for carrying on this research.

UNIVERSITY OF ALBERTA,
EDMONTON, CANADA.
July 25, 1928.

Note added Oct. 18.—The author takes this opportunity to thank Dr. C. W. Gartlein of Cornell University for allowing him the use of his very extensive measurements of the spectrum of arsenic.

A STUDY OF THE ENERGY RELATIONS IN THE HELIUM SPECTRUM

By I. Clyde Cornog

Abstract

Intensity variation at critical points in the helium spectrum.—Photographs of the helium spectrum produced in an equipotential space using an equipotential cathode have been studied photometrically in order to determine the variation of line intensities on passing the various critical potentials. The results here reported cover the 54.2 volt point, at which double ionization is first possible. Spectra were taken at suitable values between 50 and 60 volts, often at intervals of 0.1 volt. The plates show a marked maximum of intensity near 54.2 volts for all lines measured.

Introduction

ONLY a small amount of quantitative work seems to have been done on the relations between line intensity and accelerating difference of potential in helium. Among the early investigations is that of Richardson and Bazzoni.[1] Later work is that of Bazzoni and Lay,[2] and of Hughes and Lowe.[3] These investigations are all characterized by the use of non-equipotential cathodes.

The object of the present investigation is to study further the relations between the lines of the helium spectrum as functions of the accelerating difference of potential alone, particularly in the neighborhoods of the critical points of the gas. This report has to do with the 54.2 volt critical point, at which value of the accelerating P.D. the complete enhanced spectrum of helium first appears.

Apparatus

The discharge chamber is shown in Fig. 1. It is of blown quartz, with a window of optical quartz fused on at W. Projecting downward is a charcoal tube O which may be inserted into a liquid air bath. At D is a Hale-Pirani resistance pressure gauge, which was used to follow pressure changes in the gas, and next to this was a stop-cock by means of which the discharge tube could be cut off from the rest of the apparatus. The two leads L and L, of No. 14 B. & S. nickel wire, support both cathode and anode. These leads are firmly waxed to the ground stopper F, which is in turn sealed into the tube with Pizien cement. The support D for the anode K is fastened to the insulated clamp A' and is insulated with mica from both clamp and anode.

The anode and cathode are shown in Fig. 2. The cathode proper is a cylinder made of 0.005 in. (0.0127 cm) sheet nickel and is about 0.6 in. (1.52 cm) long and 0.040 in. (0.1016 cm) inside diameter. It is fastened to

[1] Richardson and Bazzoni, Nature, **88**, 5 (1916).
[2] Bazzoni and Lay, Phys. Rev. **23**, 327 (1924).
[3] Hughes and Lowe, Proc. Roy. Soc. **A104** (1923).

the heavy nickel tips of the leads L and L by means of a screw at each end, and is insulated from one tip by means of mica. This cathode has a pin stripe of a mixture of 60 percent barium oxide and 40 percent strontium oxide painted down the part of its area that faces the anode. The active substance is applied as a finely divided suspension of the hydroxides in water. The cylinder is heated by means of a tungsten wire of 0.015 in. (0.381 cm) diameter that passes axially through it. This filament is fastened to one tip by a set screw and is held straight by a small spring S on the other tip. This cathode represents the only highly successful one of several types that were tried.

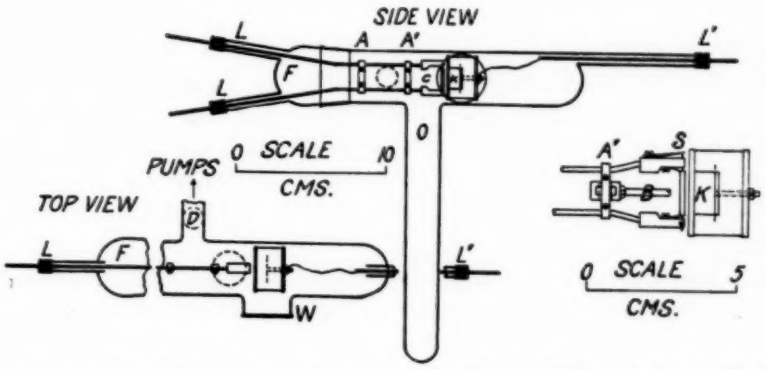


Fig. 1. The discharge chamber.

Fig. 2. The anode and cathode.

The anode K is a pill box of thin nickel. In the front of this, facing the cathode, is a rectangular opening 1.5 cm$\times$0.5 cm, which is covered with 80-mesh nickel gauze and through which electrons can pass into the box. A second opening, for spectrographic examination of the radiation within the box, is in front of the window W. The interior of the box is covered with camphor soot to prevent reflection. The window W is shielded from the visible cathode radiation by means of a shield fixed to the box. For best working conditions the anode is placed 1.25 mm from the cathode.

The spectrometer used was a Type E Hilger spectrometer giving a 30 inch spectrum. It accommodated 10-inch plates and as many as 17 spectra have been photographed on the same plate. The latter procedure gave rise to pre-exposure of the plate, which will be referred to later. The optical system was quartz throughout. The slit of the instrument was placed less than a millimeter distant from the window W, and in front of the most uniform part of the glow seen through the window K.

The microphotometer used to determine the relative densities of the line images on the plates was constructed during the investigation. It is essentially the same as that of Moll,[4] Harrison,[5] and Barnes,[6] although non-recording. Two outstanding characteristics of the instrument are the use

[4] Moll, Phys. Soc. Lond. Proc. **33** (1921).
[5] Harrison, J.O.S.A. **10**, (1925).
[6] Barnes, J.O.S.A. **15** (Dec. 1927).

of a Moll vacuum thermo-element, which gives a highly desirable instrumental stability, and the fact that the very narrow slit (0.1 mm to 0.2 mm) can be placed so that it touches the photographic film.

The precision of the instrument was entirely satisfactory. In seven absolutely independent measurements on a given line-image, the greatest difference between readings was 0.4 percent of the smallest reading. This is the greatest value of the percent error encountered in the photometric measurements. However, an examination of the literature pertaining to the use of the photographic plate for intensity measurements[7] shows that the real limitation of precision in such work is in the plate itself. With the most careful procedure the resulting precision lies between 1 and 4 percent.

Procedure

The usual high vacuum technique was employed in evacuating the system. The anode was held for a sufficiently long time at red heat by means of an induction furnace, and filament and cathode were held for several hours at a temperature considerably higher than their working temperature. Pressures of the order of 10^{-6} mm of mercury were obtained in the cleaned apparatus.

The helium used was from a lot supplied by the Bureau of Mines, the original source being natural gas. The gas was allowed to stand for 15 to 20 minutes surrounded by liquid air and was then admitted very slowly to the apparatus through a capillary tube. It passed through two charcoal traps and through two U traps, all under liquid air, into the tube, whose charcoal trap was also thus cooled. In the cases of a great many specimens of helium admitted to the discharge chamber, the presence of mercury vapor or of any other gases could not be detected spectroscopically, either before use or after many hours of use. Samples of gas have been held during use for as long as five days, always under liquid air, after which plates of as long as an hour exposure have shown no lines other than those of helium.

The procedure of exposure was as follows: Having determined the product of accelerating P.D., electron current, and time of exposure (VIT) which would give a suitable photographic plate corresponding to the conditions existing within the apparatus, the electron current was thereafter kept, by manipulation of cathode temperature, at the same value during the exposure of a plate which might have on it, finally, a dozen or more spectra, each photographed under unique voltage conditions. For each of these spectra there was an assigned value of P.D., the time of exposure being determined in such a way that the product (VIT) was the same for all. In this way the same amount of energy was supplied to the arc, and presumably to the plate, during the exposure for each of the spectra that appeared on the plate. Provided that the configuration of discharge does not change with time or with potential adjustments thus affecting the

[7] Monographs on the Theory of Photography, from the Research Laboratory of the Eastman Kodak Co., No. 5, "The Physics of the Photographic Image," F. E. Ross. D. Van Nostrand Co. (1924).
Bureau of Standards Bull. No. 439, (May 5, 1922).

luminosity of that part of the discharge in front of the spectrometer slit, and providing that other conditions including pressure remain fixed, it is assumed that the intensity of a given line in the source remains the same so long as the accelerating P.D. and the electron current remain the same.

The accelerating P.D. used varied between 50 and 60 volts. In the neighborhood of the critical point (54.2 volts) the variation was by 0.1 volt steps. Any given value, as measured with a Weston Standard voltmeter, could be held well within ± 0.1 volt. The voltmeter of course measured the total P.D. between its terminals, which might be different from the accelerating P.D. To determine the true value of the latter the relation between voltmeter reading and electron current in the neighborhood of the 24.5 volt ionization point was plotted. In this curve a sharp break occurs at the ionization point, and the difference between the accepted value of this P.D. and the break-point value shown on the curve gives the total voltmeter correction for the particular cathode arrangement used. There seems to be no reason to suppose the correction at 24.5 volts to be different from that at 54.2 volts. This correction for the particular cathode described here was 0.0 volts, the possible error being considerably less than ± 0.1 volt.

It was found that if the conditions of the initial exposure were repeated at intervals during the production of a plate having on it several spectra, the corresponding measured values of the intensity of a given line fell off progressively in value. It would seem, therefore, that the measured intensities of all lines need some correction in order to give the true values. To determine this correction the conditions of the initial exposure on any particular plate were repeated five times during a run of, say, sixteen exposures. The difference between the measured intensity of any one of these repeated values and that of the initial value gave the correction to be applied in order to get the true value of the intensity of the line under consideration. The time from the beginning of the first exposure to the mid-point of each individual exposure was known. The above corrections plotted against the corresponding times from the start gave a correction curve for the particular wave-length in question. To get the correction for a given line image, it was necessary only to use its time of exposure referred to the start in conjunction with its particular correction curve. These corrections varied up to 25 percent of the measured value of the intensity in the case of plates during the exposure of which the arc ran for two hours. For a plate of six hours arc time the correction might be as high as 100 percent of the measured intensity.

This effect was at first ascribed to change in gas pressure, but tests made with the Hale-Pirani[8,9] resistance pressure gauge showed no changes of pressure as great as 1 percent of that within the tube. Neither could the effect be due to the decay of the active cathode deposit, since the electron current was maintained at a constant value. It was finally shown conclusively that the effect is due to exposure of the plate in the spectrometer

[8] High Vacuum, S. Dushman, Pub. by General Electric Review (1922).
[9] Skellett, J.O.S.A. 15, (July 1927).

to light scattered or reflected over its face outside the zone of the principal image. The net effect of this pre-exposure is equivalent to a progressive decrease of plate sensitivity with time. This observation has an important bearing on the use of spectrometers of this kind for photometric work in all cases where there is a possibility of scattering of light over the face of the plate. Our tests show that this difficulty is effectively remedied by the use of a light-proof diaphragm placed directly against the emulsion in such a way as to permit exposure of only one part of the plate. These diaphragms were not used in the work upon which this report is based. It seems, however, entirely legitimate to apply the correction curves as above described to the observed line densities.

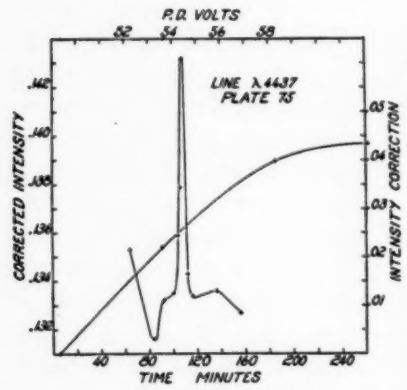
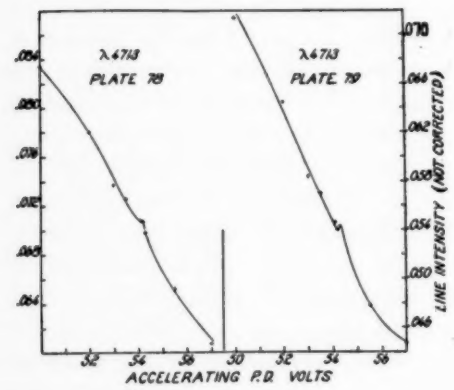


Fig. 3. A typical correction curve and the corresponding corrected curve for the variation of intensity of a spectral line with voltage.

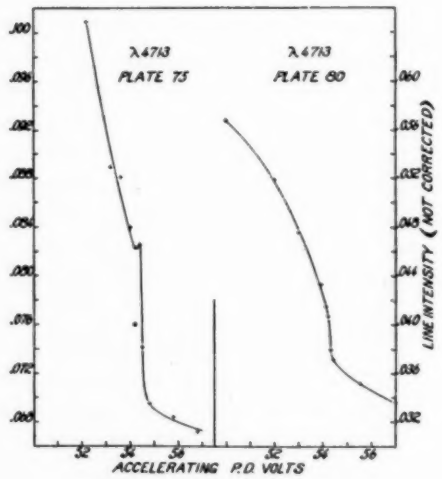
The corrected values of the intensity of each spectral line having been obtained (all for the same wave-length), these were plotted against the corresponding corrected accelerating potential differences. Fig. 3 shows a typical correction curve and the corresponding corrected curve. Figs. 4A and 4B show typical uncorrected curves.

So far most of the photographs have been made on Eastman "Speedway" plates. Time development was carried out according to data for "Rodinol," the developer used, and the tray was rocked throughout.

The gas pressure at which this work was done was 0.33 mm of mercury, which was read on a McLeod gauge.



4A

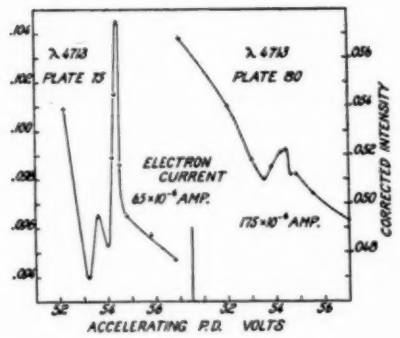


4B

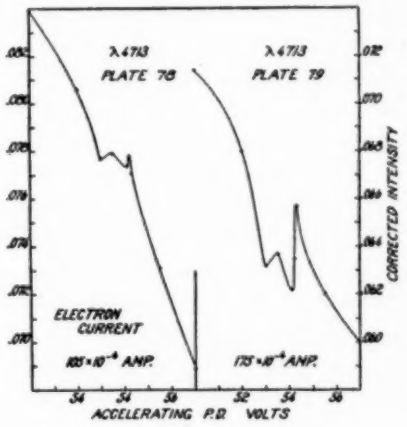
Figs. 4A, 4B. Typical uncorrected curves.

RESULTS

A study of the spectral line λ4713A as it appears on four different plates is shown in Figs. 5A and 5B. These plates are independent in every way, with the exception that the same sample of gas was used for plates 75 and



5A



5B

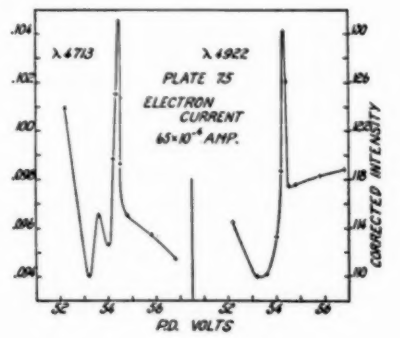
Figs. 5A, 5B. Variation of intensity of λ4713A with voltage.

78, although these were taken on different days. The curves are plotted between line intensity corrected as explained above and the corresponding accelerating potential differences.

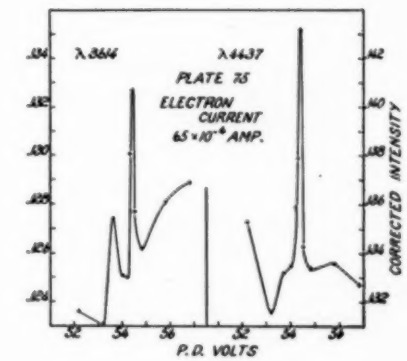
Figs. 6A and 6B show a group of characteristic corrected curves, all from plate 75 and for the lines

λ4922 $(1P-mD)$	λ4713 $(i\pi-m\sigma)$
λ3614 $(1s-mP)$	λ4437 $(1P-mS)$

All these curves show well defined maxima in the neighborhood of the 54.2 volt point.



6A



6B

Figs. 6A, 6B. Variation of intensity of λλ4922, 3614, 4713, and 4437 with voltage.

It is difficult at the present time to offer any adequate theoretical explanation relating these intensity changes to the contributory causes. The changes are, in part at least, dependent upon the number of atoms per cubic centimeter, the number of states of ionization existing coincidentally among the atoms, and the distribution of kinetic energy among the impinging electrons. When the accelerating P.D. is the critical one of 54.2 volts, the spectrum intensity relations are further complicated by the energy distribution in the newly appearing enhanced series. The remarkable peak that occurs in these intensity curves at this critical P.D. has to do with the sudden rearrangement of spectral energy relations and is apparently significant. Just what its significance is, however, does not appear at the present stage of the investigation.

The curves in Figs. 4A and 4B, all for the line λ4713A, are plotted from the same original measurements as are the curves in Figs. 5A and 5B but without correcting the photometer measurements as described above. It will be noted that on plates 75 and 79 well defined maxima are nevertheless observable in the neighborhood of the 54.2 volt point. Plates 78 and 80 admit of the possibility of such maxima, but these plates were unsatisfactory, first, because the points were not chosen in such a way as to show a maximum if such did exist, and second, because the respective correction curves show that the conditions within the tube during the exposure were not steady. It might be remarked at this point that the correction curve represents a net effect consisting of at least two components, viz., the pre-exposure effect commented upon above, which probably follows some logarithmic law, and any accidental fluctuation in the intensity and configuration of the arc. Even so, there is in each of these curves a well defined change of slope at the 54.2 volt point.

The work and results described in this report were first presented under the same title at the Washington, D. C., meeting of the American Physical Society, April 28 and 29, 1928.[10]

In conclusion, I wish to express my appreciation of the unremitting labor of my colleague, Mr. J. T. Lay, and of the equally sincere and helpful interest of Professor C. B. Bazzoni.

RANDAL MORGAN LABORATORY OF PHYSICS,
UNIVERSITY OF PENNSYLVANIA,
May 1, 1928.

[10] Cornog, Lay, and Bazzoni, Phys. Rev. 31, 1109 (1928).

THE FINE STRUCTURE OF THE SHARP SERIES TRIPLET, $2^3P_{0,1,2}-2^3S_1$, OF OPTICALLY EXCITED MERCURY RADIATION

By E. Hobart Collins

Abstract

Measurements on the fine structure of the sharp series triplet, lines of wave-lengths λλ5461, 4358 and 4047 were made with two Lummer-Gehrcke plates under two conditions of optical excitation. The first condition of optical excitation was obtained by having mercury vapor only in the resonance tube, giving excitation by absorption of λ4358, the second by having mercury vapor with nitrogen present at a pressure of 2 to 4 mm, giving excitation by absorption of both λ4358 and λ4047. For the first condition of excitation the wave-length differences in milli-angstroms are for λ5461, $d\lambda 0$; for λ4358, $d\lambda -157$, -107, -20, 0, $+30$, $+46$, $+183$; for λ4047, $d\lambda -116$, -62, -52, 0. For the second condition the wave-length differences are for λ5461, $d\lambda -235$, 0; for λ4358, $d\lambda -107$, -20, 0, $+30$, $+183$; for λ4047, $d\lambda -110$, -62, -53, 0. Certain fine structure energy differences of interest in the construction of energy diagrams are pointed out but it was not found possible with the data available to construct a complete energy diagram of the triplet. A comparison of the fine structure observed under the two conditions of optical excitation with one another and with the fine structure of the arc shows striking differences which make it evident that differences in fine structure exist which depend on the method of excitation.

Introduction

THERE is at present no theory which offers a completely satisfactory explanation of the fine structure of the spectral lines. Ruark and Chenault[1] have proposed the introduction of a fifth or fine quantum number and a selection principle to account for certain fine structures. However, they have proposed no kinematical interpretation of this fine quantum number, unless we accept a vague suggestion that it may be associated in some way with differences in configuration of the underlying electron shells. More recently MacNair[2] and Fraulein Schrammen[3] have devised energy levels which account in a satisfactory way for their observations on the fine structure of a large number of cadmium lines. These level schemes, however, have not been unique and at present there is no way of deciding among the various possibilities.

Pauli[4] has suggested that an appropriate moment associated with the nucleus of the atom may account for some types of fine structure. He has also pointed out that such a model would imply the existence of phenomena of the same nature as the Paschen-Back effect, and in support of this has cited Nagaoka's observations on the Zeeman effect of the $2^3P_{0,1,2}-2^3S_1$

[1] Ruark and Chenault, Phil. Mag. **50**, 937 (1925).
[2] MacNair, Phil. Mag. **2**, 613 (1926).
[3] Schrammen, Ann. d. Physik **83**, 1161 (1927).
[4] Pauli, Naturwissenschaften **12**, 741 (1924).

mercury triplet. Back and Goudsmit[5] have shown that the fine structure of the bismuth spectrum and its very complex Zeeman effect may be successfully accounted for if it is assumed that the bismuth nucleus possesses a mechanical moment of $(9/2)(h/2\pi)$. It does not appear, however, that the fine structure of the mercury spectrum is to be accounted for in this way. Goudsmit[6] has pointed out that on the nucleus spin hypothesis λ2537 should have at most three components and that these should show three types of Zeeman effect in weak fields. Actually the line has five components, three of which show a 3/2 normal Zeeman effect.

The primary object of the present investigation was to learn whether fine structure patterns could be made to vary by changing the method of excitation. It was not expected that the method used would be adapted to accurate determination of wave-length differences, because of the long exposures required and the impairment of definition in the interference patterns of the Lummer-Gehrcke plates occasioned by slight and almost unavoidable temperature changes. The results of Nagaoka[7] (the data used by Ruark[8]) for the fine structure of these lines in the ordinary arc were accepted, and an attempt was made to identify the various components observed with one or another of the accepted patterns. In general this succeeded very well, the observed wave-length differences agreeing quite closely with those found by Nagaoka.

The possibility of different methods of excitation was provided by some beautiful experiments of Fuchtbauer,[9] upon the optically excited spectrum of mercury. These experiments were later greatly amplified and extended by R. W. Wood,[10] who showed, for example, that there were several ways of raising an electron to the 2^3S_1 level by optical means. The experiments now presented show that the fine structure of the lines emitted when the electron falls to the $2^3P_{0,1,2}$ levels are different for the different ways in which the electron may be raised to the 2^3S_1 level initially.

The two conditions of optical excitation, under which the fine structure of the $2^3P_{0,1,2}-2^3S_1$ triplet has been observed, are:

A. Absorption by mercury vapor in the absence of any foreign gases;

B. Absorption by mercury vapor in the presence of nitrogen at a pressure of from 2 to 4 mm of mercury.

Under the condition A the 2^3S_1 level is reached by the absorption of λ2537 followed by the absorption of λ4358. Absorption of λ4047 and λ5461 is negligible.[10]

Under condition B some electrons reaching the 2^3P_1 level are spilled over into the 2^3P_0 level by collision with nitrogen molecules and the concentration

[5] Back and Goudsmit, Phys. Rev. **31**, 1125 (1928).

[6] Letter from Dr. S. Goudsmit.

[7] Nagoaka, Proc. Phy. Soc. London, **39**, 91 (1917).

[8] Ruark, Phil. Mag. **1**, 980 (1926).

[9] Fuchtbauer, Phys. Zeits. **21**, 635 (1920).

[10] Wood, Proc. Roy. Soc. **A106**, 679 (1924); Phil. Mag. **50**, 774 (1925) and Phil. Mag. **4**, 466 (1927).

of atoms in this metastable state becomes great enough that the absorption of λ4047 is as great or greater than that of λ4358. Absorption of λ5461 is still negligible. Under this condition, then, electrons reach the 2^3S_1 level from either the 2^3P_1 or the 2^3P_0 level. There is also evidence[11] that some electrons may reach the 2^3S_1 level directly from the 3^3D levels and it appears that this process plays an important role in the interpretation of results.

Apparatus

The general arrangement of apparatus is shown in Fig. 1. The resonance tube *A* was a quartz tube one inch in diameter and about six inches long, sealed by a graded seal to a Pyrex tube of the same diameter. It was made horn shaped to minimize reflected light and was painted black except for a two inch space which admitted light from two mercury arcs. Self reversal of the lines emitted by the exciting arcs was avoided by water-cooling these and by forcing the discharge close to their walls by means of two small magnets. The end of the resonance tube was sealed by a carefully polished disk of fused quartz cut to fit the inner diameter of the tube. By means of a pointed oxygen-hydrogen flame the walls of the tube and the end of the disk were heated and fused together. Care was taken to keep the center of the inner surface of the quartz plate undisturbed and free from any deposit of oxide caused by the hot flame. After the seal was made and tested, the outside of the quartz was ground and polished again.

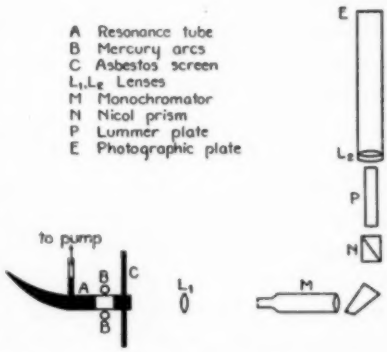


Fig. 1. Arrangement of apparatus.

The end of the tube was painted black except for an aperture of such size that no scattered light from the walls of the tube could enter the lens L_1 which focused the light on the collimator. An asbestos screen *C* kept direct light from the arcs from entering the rest of the apparatus.

The optically excited radiation was focussed on the collimator slit of a Hilger monochromator *M*. For most of the measurements the lens and slit of the telescope were removed and the parallel beam of light from the prism of the monochromator passed directly through a nicol prism into the Lummer-Gehrcke plate. A less satisfactory method was to use the telescope and second slit of the monochromator, with a cylindrical lens placed at its focal distance from the slit with its axis parallel to the slit, so that it rendered the emergent rays parallel in the plane of the Lummer-Gehrcke plate and made possible the focussing of the slit of the monochromator on the photographic plate.

The Lummer-Gehrcke plate was placed in a horizontal position with just sufficient tilt to bring the maximum of intensity into the lower orders

[11] Wood, Phil. Mag. **4**, 480 (1927).

of the interference pattern. Back of the Lummer-Gehrcke plate an achromatic lens focussed the light onto a photographic plate. The Lummer-Gehrcke plate and camera were rigidly mounted on a five inch "I" beam.

The Lummer-Gehrcke plates were those used by Ellett and MacNair.[12] Their thicknesses and order separations are given in Table I below.

TABLE I. *Data relative to the Lummer-Gehrcke plates.*

Plate	Thickness (cm)	Order separations λ5461	λ4358	λ4047
1	0.642	0.189A	0.117A	0.101A
2	0.492	0.248A	0.153A	0.131A

All the apparatus was mounted in a constant temperature room. For exposures of less than six hours the extreme variation in temperature of the room was less than 0.2°C; for exposures of twenty to thirty hours, the extreme variation in temperature was less than 0.4°C. The Lummer-Gehrcke plates were insulated by several coverings to damp out the small temperature fluctuations, and their temperature, inasmuch as sharp lines were obtained certainly varied much less than that of the room.

RESULTS AND DISCUSSION

The data obtained for both conditions of excitation for the lines λ5461, λ4358 and λ4047 are given in Tables II, III and IV. The use of two Lummer-Gehrcke plates with different thicknesses made possible the determination, with considerable accuracy, of the wave-length differences. The interpretations are made more certain since, as mentioned above, we expect the components observed in the optically excited radiation to have nearly the same wave-length as those observed in the mercury arc. For purposes of comparison the fine structure of the mercury arc as observed by Nagoaka[7] is given in the first column. The intensities are merely visual estimates.

TABLE II. *Data for* λ5461.

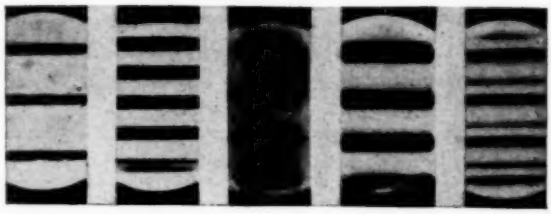
Arc	Condition A			Condition B		
$d\lambda$ Milli-Angstroms	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}
−237				10	−235	+785
102						
70						
47						
19.9						
8.4						
0		Single		10	0	0
8.2						
18.4						
85						
128						
214						

[12] Ellett and MacNair, Proc. Nat. Acad. 13, 583 (1927) and Phys. Rev. 30, 180 (1928).

In Table II are given the results for the green line λ5461. This line under condition A is single; a surprising result when we consider that the fine structure of the arc line shows 12 components. A thirty-one hour exposure of a film sensitized for green by an erythrozine dye[13] gave a sharp, intense and over-exposed single component but failed to reveal other components.

In condition B there were two components of about equal intensity with a wave-length difference of 0.235A, and since this agrees within experimental error with the difference between 0 and −0.237A components of the arc, these values were assigned. The single component of condition A is then very probably the zero component of the arc line. On one spectrogram only two very weak components which could not be assigned a definite wave-length were observed. These latter may have been due to peculiar conditions existing in the source of light or possibly to a small amount of stray light.

The results for λ4358 are given in Table III. It appears from this table that only a few of the components observed in the fine structure of the mercury arc line λ4358 appear in the fine structure of the optically excited line. Most of those observed agree closely in wave-length with the published



a b c d e

Fig. 2. Enlargements of selected spectrograms.

measurements of the arc line. The wave-length differences assigned to the components of λ4358 in condition B are the result of measurements taken with the thin Lummer-Gehrcke plate only, the selection of wave-length differences being made so as to account for the overlapping of orders on the spectrogram taken with the thick Lummer-Gehrcke plate. (See Fig. 2d.)

The Lummer-Gehrcke patterns for λ4047 taken under the two conditions of excitation show the same lines. The measurements are given in Table IV.

Five enlargements of selected spectrograms are presented in Fig. 2. Spectrograms *a* and *b* show the appearance of the green line, λ5461, under the two conditions A and B respectively. The spectrogram *b* showing the 0 and −0.235A components was taken with the thicker Lummer-Gehrcke plate, with an order separation for λ5461 of 0.189A. With the thin Lummer-Gehrcke plate having an order separation of 0.248A the components were close together, appearing as one broad line. Spectrograms *c* and *d* show

[13] Baly, Spectroscopy Vol. II, p. 373; see also Derr, Photography for students of Physics and Chemistry, p. 102.

the appearance of λ4358 taken with the thick Lummer-Gehrcke plate under the A and B conditions of excitation. When due allowance is made for different times of exposure and different light intensity of the source it is

TABLE III. *Data for λ4358.*

Arc	Conditions A			Condition B		
Milli-Angstroms	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}
−238						
206						
160	2	−157	+.827			
108	2	107	0.560	*	−107	+.560
95						
47						
21	4	20	0.105	*	20	0.105
9						
3						
0	10	0	0	*	0	
+3						
19						
29	1	+30	−.160	*	+30	−.160
46	4	46	0.244			
108						
159						
182	3	183	0.956	*	183	0.956
224						
238						

* Due to over-lapping of orders estimated intensities uncertain.

quite evident that the intensities ratios have changed. The spectrogram *e* shows the appearance of λ4047 under condition B taken with the thin Lummer-Gehrcke plate. Only one enlargement of the spectrogram is shown

TABLE IV. *Data for* λ4047

Arc	Condition A			Condition B		
Milli-Angstroms	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}
−116	1	−116	+.708	1	−116	+.708
61.4	2	62	0.378	2	62	0.378
47.5	5	53	0.330	5	53	0.330
12.3						
3.9						
0	10	0	0	10	0	0
+4.1						
59.2						
117.0						

since the only change in λ4047 under the two conditions of excitation was a slight change in the relative intensities.

Fine Structure Energy Levels

Ruark[8] has given an excellent critical summary of the existent data for the fine structures of a large number of lines of the mercury arc, including λλ5461, 4358, 4047 and also λλ3663.28, 3654.83, 3650.15, 3663.05, 3131.56 and 2967. His proposed fine structure energy levels do not account for all of the fine structure components of these lines, but they do point out the existence of energy differences common to the several lines. So many of the observed fine-structure components fit into his level scheme that it seems reasonable to assume that these levels actually exist and that it would be possible to account for the remaining components by the introduction of a few additional levels, if the wave-lengths of these components were only known with the requisite accuracy. If it is assumed that this incomplete level scheme is valid as far as it goes, certain conclusions are evident. For example, absorption of either λ4358 or λ4047 should excite fine-structure levels of 2^3S_1 from which arise no less than nine components of λ5461. Now actually, as has been pointed out above, the situation is quite different, λ5461 having sometimes but one and sometimes two components when excited by absorption of these lines.

An attempt has been made to find a set of levels which would account for the existence of the fine-structure components of λλ5461, 4358 and 4047 observed in the optically excited spectrum. The fine structure of λ2537 is known to be the same when excited in resonance radiation as in the arc[14] so that we may be certain that none of the five components ascribed to this line are due to self-reversal or other perturbing causes. A frequency difference of 0.160 cm^{-1} is common to λ4358 and λ2537 and the difference 0.349 cm^{-1} found in λ4358 may be the same as 0.345 cm^{-1} observed in λ2537.

The introduction of frequency differences of 0.330 cm^{-1} into 2^3P_0 and of 0.375 cm^{-1} into 2^3S_1 accounts satisfactorily for all of the components of λ4047 in the optically excited radiation. McCurdy[15] finds a frequency difference of 0.330 cm^{-1} in λ2967, $2^3P_0-3^3D_1$.

There is obviously no way of deciding which level of 2^3S_1 gives rise to the single component of λ5461 observed under condition A, nor does the difference of 0.785 cm^{-1} between the two components observed in condition B appear in either λ4358 or λ4047. The introduction of nitrogen (condition B) does not give rise to any new components in λ4047 so that there is no reason to say that the absorption of this line in condition B causes the excitation of levels of 2^3S_1 not reached by any component of λ4358. The emission of an additional component upon admission of nitrogen is probably due to some process which gives rise to emission of λλ5461, 4358 and 4047 when mercury vapor in the presence of nitrogen is excited by bromine and chlorine filtered radiation from which these three lines are absent. Wood points out that this may be brought about by spilling electrons from the 3^3D levels

[14] Ellett and MacNair, Phys. Rev. **31**, 180 (1928).
[15] McCurdy, Proc. Nat. Acad. Sci. **13**, 701 (1927).

to 2^3S_1 or by collisions of the second kind with excited nitrogen atoms or molecules carrying electrons up from the 2^3P levels to the 2^3S_1.[11]

Conclusion

Lummer-Gehrcke spectrograms of the fine structure of the sharp series triplet taken under two conditions of optical excitation show striking differences and a fine structure different from that of the arc lines; establishing experimentally that the fine structure of a spectral line depends upon the method of optical excitation.

The writer wishes to express his sincere appreciation to Dr. A. Ellett who suggested the problem and who was a constant source of help and encouragement during the course of the investigation.

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August 11, 1928.

THE ASSIGNMENT OF QUANTUM NUMBERS FOR ELECTRONS IN MOLECULES. II. CORRELATION OF MOLECULAR AND ATOMIC ELECTRON STATES

By Robert S. Mulliken

Abstract

A few revisions, suggested by recent results of Herzberg on N_2^+, are made in Table III of I, for N_2^+, CN, and O_2^+. These revisions involve dissociation of unexcited molecules to give one excited atom or ion. With these revisions, and a revised heat of dissociation for N_2, the quantum number assignments previously made are found to be all consistent with Hund's rule of σ_l and s sums, and, except for one or two states of F_2, with the σ_{l_τ} *conservation rule* given in I. This result gives needed support to the latter rule. The probable atomic *dissociation products* are determined for most of the molecular states given in Table III of I. In the cases of N_2 and N_2^+ the probable dissociation products and energies are given in Table I. An interpretation is given of the dissociation processes involved in Hogness and Lunn's NO ionization potentials at 21 and 22 volts, and of their 24 volt N_2^+ potential. Evidence is brought forward for a revision of Birge and Sponer's values of the *heats of dissociation* for the normal states of several molecules, in particular N_2. Suggested new or revised values are, in volts, N_2, 9.5; N_2^+, 7.1; NO, 7.3; CO^+, 8.3; NO^+, 11.2. The alkali and hydrogen halides are briefly discussed with reference to their electronic states and dissociation products.

Introduction

IN a previous paper, which in the following will be referred to as I,[1] tentative electronic quantum number assignments were made for a number of molecular states. In the present paper an attempt is made to determine so far as possible the electronic states of the atomic products which would result by dissociation from each such molecular state. The conclusions in regard to this correlation have already been summarized in Table III of I. A few changes in these conclusions are given below for N_2^+, CN, and O_2^+.

Hund[2] has previously discussed briefly the correlation of atomic and molecular states for the molecules BO, CN, CO^+, N_2^+, and CO, making use of the rule that σ_l and s of the molecule must be obtainable from σ_l and s of the atoms by algebraic or vector addition, and that there is a one to one correspondence between molecular states and atomic states.[3] In addition to these rules of Hund, we may often or perhaps usually expect σ_{l_τ} for each electron to be preserved in the formation of the molecule (σ_{l_τ} conservation rule). Reference should be made to the section in I entitled "Correlation of molecular quantum numbers with those of separate atoms" for further details in regard to the meaning and method of application of these rules.

[1] R. S. Mulliken, Phys. Rev. **32**, 186 (1928).

[2] F. Hund, Zeits. f. Physik **42**, 93 (1927).

[3] As Hund remarks, some of the predicted molecular states may be very unstable, but it seems hardly justifiable to say, as Heitler and London appear to do, that these are not real molecular states.

The specific problem here considered is as follows: given a molecular state of known type and configuration, into what states of atoms or ions would it dissociate on increasing the vibrational quantum number? The solution of this problem in any individual case suffers from difficulties of various kinds. (1) In the first place, the molecular configurations given in Table III of I are all more or less uncertain, while in many cases even the molecular state (as ^2D) is not sure. For this reason one of the *objects* of the present paper is to investigate whether the assignments made in Table III of I are consistent with the dissociation products which are called for by the rules discussed in the preceding paragraph. (2) Another difficulty is that one of these rules, the σ_l, conservation rule, has no sure theoretical basis; hence another of the *objects* of the present paper is to investigate the extent to which this rule is consistent with known data; the result of this investigation, it may be well to state at once, is that there seem to be only two examples (^1S states of F_2) which definitely conflict with this rule. (3) A further difficulty in testing the theory is that in most cases not just *one* but a considerable number of molecular states of a given type and configuration class are to be expected from the union of normal or slightly excited atoms; e.g., s^1p^4, ^3S states of N_2 should be formed as follows from N atoms[3,4]: one from $N(^4S)+N(^4S)$; one from $^4S+^2D$; one from $^4S+^2P$; three from $^2D+^2D$; three from $^2D+^2P$; one from $^2P+^2P$. To make possible the definite correlation of a particular observed s^1p^4, ^3S state with its dissociation products, supplementary evidence is needed. An accurate knowledge of relative energy levels and dissociation energies (D^v) for observed states, together with a definite knowledge of the dissociation products of at least one state of N_2, would evidently serve this purpose, and it is in fact to such data that we chiefly turn for empirical evidence here and in the matters just mentioned in (1) and (2). Unfortunately, however, the D^v values are for the most part rather uncertain. (For exact definitions of D and D^v, cf. Table III of I, note 7.)

A helpful principle in combating the difficulties just mentioned is that, in a general way, the lowest states of a molecule may be expected to be derived from the lowest states of the atoms. For example, if one had to determine the dissociation products of the *lowest* s^1p^4, ^3S state of N_2, the most likely guess, in the absence of other evidence, would be that it is derived from two ^4S atoms; similarly, for the next higher s^1p^4, ^3S state the best guess would probably be a ^4S plus a ^2D atom (cf. above). The usefulness of this method is, however, obviously weakened by the fact that in practise our empirical knowledge of the energy levels of molecules is very incomplete; thus in the present instance, conclusions in regard to *observed* s^1p^4, ^3S levels would be uncertain if other undiscovered levels of this kind might exist.

Furthermore, the method is also on theoretical grounds an uncertain one, since the energy curves $E(r)$ for two molecular levels of a given type may sometimes cross or tend to cross. As a result, the energy order of the *molecu-*

[4] These results can be deduced by means of Table II of I.

lar levels (at $r=r_0$) may be different from the order of the correlated *atomic* levels ($r=\infty$); or else, as Hund as shown,[5] the correlation of the molecule with the separate atoms may be ambiguous, i.e., a molecule in a particular state may dissociate with a certain probability in each of two or more ways. The possibilities of reversal of energy order and of ambiguous correlation may be illustrated by considering the normal state of HF. This is a ^1S state with probably a Ne-like electron configuration of the s^6p^4 class. Such a state would be expected from the union of an H atom (^2S, s^1 class) and an F atom ($^2S^p$, s^5p^4 class, cf. Table II of I), but another state of the same kind would be expected from the union of an H^+ ion and an F^- ion ($F^-=^1S$, s^6p^4). Although H^++F^- represents a higher energy than H+F, it is nevertheless likely that the normal state of HF is derived from H^++F^-, according to Pauling[6]; in this case the s^6p^4, ^1S state of HF which is derived from the atoms must be an *excited* (possibly unstable) state. Or it may be that in HF we have an example of ambiguous correlation, so that *each* of the two ^1S states mentioned dissociates with a certain probability into either atoms or ions. Questions of this kind have been discussed in recent papers by Hund,[5] London,[6] and Pauling.[6]—Similar ambiguities of correlation and reversals of energy order are also expected in other cases where the choice is not between atoms and ions, but between different states of the same atoms. For example, the normal, s^2p^4, ^2S, state of N_2^+ probably gives an N^+ ion and an *excited* N atom on dissociation, while the first excited s^2p^4, ^2S state probably gives an *unexcited* atom and ion (see below).

Discussion of Examples

The discussion of individual examples given in the following paragraphs is subject to the limitations and uncertainties described in the preceding section, and the conclusions reached are in most cases more or less tentative. The general procedure is to make a list of the molecular states, derived from each possible combination of low-lying atomic states, making use of Table II of I for this purpose, then to compare this list of predicted states with the list of observed molecular states; then to make identifications between the two lists, so far as is possible with the help of the criteria already discussed.

Li_2. Two unexcited Li atoms (each s^3, $^2S^S$) should give an s^6, ^1S and an s^6, ^3S Li_2 molecule. The lowest possible s^6, ^1S state of Li_2 must almost certainly be a $(1s^s)^2(2s^p)^2(2s^s)^2$ state, as assumed in Table III of I, and this is doubtless the normal state of Li_2. (Such a state is not yet known experimentally for Li_2, but a corresponding state is known for the analogous Na_2.) For the lowest possible s^6, ^3S state of Li_2 one of the $2s^s$ electrons of the ^1S state just mentioned must evidently be promoted to a $3s^p$ or $3s^s$ (or possibly $3s^d$) orbit (cf. BeO and C_2, Table III of I). This ^3S state must then be one with a small D^v, and it may be related to the ^1S state much as the 2^3S state of H_2 formed by two normal H atoms is related to the 1^1S normal state of H_2

[5] F. Hund, Zeits. f. Physik **40**, 742 (1927).

[6] F. London, Zeits. f. Physik **46**, 455 (1928); L. Pauling, Proc. Nat. Acad. Sci. **14**, 359 (1928).

(cf. "discussion of Heitler and London's work" in I). Heitler, approaching the matter from a different viewpoint, has reached essentially this conclusion.[8]

LiF, BeO, *alkali halides*, BeF. From unexcited Li+F we expect the following states of LiF: ^3S and ^1S, both s^8p^4, from $\mathrm{Li}(s^3;\ ^2S^S)+\mathrm{F}(s^5p^4,\ ^2S^P)$, and ^3P_i and ^1P, both s^9p^3, from $\mathrm{Li}(s^3,\ ^2S^S)+\mathrm{F}(s^6p^3,\ ^2P^P)$. From normal $Li^+ + F^-$ we expect only a ^1S, s^8p^4 molecule of LiF, since we have $\mathrm{Li}^+(s^2,\ ^1S) + \mathrm{F}^-(s^6p^4,\ ^1S)$. Normal LiF ($s^8p^4$, ^1S according to Table III of I) is probably derived from $Li^+ + F^-$ (cf. discussion of NaCl and other alkali halides by Hund[5] and London[6]), while the four states derived from unexcited Li+F are probably excited states of LiF.

The relations for LiF are probably typical for the alkali halides. The continuous absorption spectra shown by these molecules in the ultra-violet[6a] probably represent jumps from the normal, ionic, state to the dissociation continua associated with these four excited states and with others involving an excited alkali atom as a dissociation product. These excited states are evidently all relatively unstable, since the continuous character of the absorption shows, according to Franck's theory, that the most probable jump is that to a condition of dissociation.

Of the two observed, presumably low-lying, ^1S states of BeO (cf. Table III of I) one may perhaps be derived from $Be^{++}+O^{--}$ and be analogous to the s^8p^4, ^1S state of LiF from $Li^+ + F^-$, and the other may be derived from $Be^+ + O^-$ and be analogous, except for greater stability, to the ^1S of LiF derived from Li+F. Probably neither one is derived from neutral Be+O, especially since one or both atoms would have to be excited in order to yield a ^1S molecule (cf. Table II of I).

The supposed ^2S normal state of BeF (Table III of I) may perhaps be derived from Be^+ (like Li) and F^- (like Ne).

C_2 *molecule.* For the Swan band emitter C_2 two ^3P states are known, both of an s^9p^3 class according to Table III of I. Two normal (^3P) carbon atoms are capable of yielding one ^3P molecular state of this class, while for the other ^3P we must assume at least one excited atom (^1D or ^1S). The possible correlations are numerous; the most plausible guess is given in Table III of I.

BO, CO^+, CN, N_2^+. Hund has already discussed these molecules,[2] and has concluded that all of the three known states (s^9p^4, ^2S; $s^{10}p^3$, ^2P_i; s^9p^4, ^2S, in order) of BO and C^+O may be formed from normal atoms. For the analogous states of CN and N_2^+ he reached similar conclusions, except that one ^2S state should have D at least 2.39 volts higher (corresponding to excitation of an N atom from ^4S to ^2D) than the ^2P_i and the other ^2S state. Hund, of course, did not consider the question of configuration class. In many cases this factor would affect the results, but as will be seen from the following, its consideration does not alter his conclusions here.

Normal B (or C^+) plus normal O gives the following possibilities (cf. discussion of B+O in I, preceding Table II): $s^{11}p^2$, ^4S, ^2S; $s^{10}p^3$, ^4P, ^2P, ^4P, ^2P;

[6a] Cf. H. Sponer, Ergebnisse der exakten Naturwissenschaften 6, 97 (1928). J. Springer.

$s^2p^4, {}^4D, {}^2D, {}^4S, {}^2S, {}^4S, {}^2S$. All three states of BO (or CO^+) may be identified with members of this group, although the possibility exists that one or more of them (in particular, the excited ^2S state) should be identified with states correlated with a slightly excited O atom.

It is possible that some or all of the states of CO^+ should be correlated with $C+O^+$ (analogous to C+N), but the correlation with C^++O seems more likely, since, as Mecke has emphasized,[9] the CO^+ electron levels parallel those of BO rather than CN. Birge and Sponer,[7] however, using the relation $D^+=D+I_a-I_m$, where D^+ is D for CO^+, D is that for CO, and I_a and I_m are the respective ionization potentials of atom (C or O) and molecule (CO), have concluded that the observed D^+ values (9.3 to 9.8 volts, according to extrapolations made by Birge and Sponer for the three states of CO) support the correlation $C+O^+$. Assuming $CO\rightarrow CO^+\rightarrow C+O^+$, we have $D^+=11.2+13.6-14.2=10.6$ volts; while if $CO^+\rightarrow C^++O, D^+=11.2+11.3-14.2=8.3$ volts; here the value $D=11.2$ is used (cf. discussion of CO below), while $I_m=14.2$, and $I_a=11.3$ for C and 13.6 for O.[10] Since the observed D^+ values (9.3–9.8 volts)[7] lie between the calculated values for C^++O and $C+O^+$, they evidently do not suffice to decide between the two possibilities.

Normal C (or N^+) plus normal N yields only $s^2p^3, {}^6P, {}^4P, {}^2P$, and $s^2p^4, {}^6S, {}^4S$, and ^2S. This is capable of accounting for *one* of the two ($s^2p^4, {}^2S$) states of CN (or N_2^+), and for the $s^2p^3, {}^2P$ state of CN. The *other* $s^2p^4, {}^2S$ state of CN (or N_2^+) must then involve at least one excited atom; very likely it is derived from a normal C (or N^+) atom, and a ^2D, or possibly a ^2P, excited N atom. According to recent conclusions of Herzberg[11] on the D' values for the two ^2S states of N_2^+, it appears that it is the *normal* state which dissociates to give an ion and ^2D excited atom, while the *excited* ^2S state dissociates to give the normal atom and ion (cf. Table I below). There is also evidence for similar relations in the case of CN.[11a]

The above empirical evidence that the lowest electron level of N_2^+ is not derived from the lowest levels of the dissociation products N^++N is important in giving us warning that similar reversals of energy order may occur in other cases.

Nitrogen. In their work on heats of dissociation, Birge and Sponer,[7] by linear extrapolation from the vibrational levels for the lowest electronic state (X) of N_2, obtained the value 11.75 volts[12] for the heat of dissociation (D_X) of this state. The similar value (11.9 volts) obtained for state A gave

[7] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

[8] W. Heitler, Zeits. f. Physik **46**, 47 (1927).

[9] R. Mecke, Naturwiss. **13**, 698 (1925); Zeits. f. Physik **36**, 797 (1926).

[10] Ionization potentials, oxygen, cf. J. J. Hopfield, Astrophys. J. **59**, 114 (1924); carbon, I. S. Bowen, Phys. Rev. **29**, 231 (1927).

[11] G. Herzberg, Ann. d. Physik **86**, 189 (1928).

[11a] Herzberg, ref. 11, p. 206, footnote 2. According to recent data of Jenkins on the violet CN bands, it appears that D' and D for the excited ^2S state of CN should be considerably reduced as compared with the values given in Table III of I.

[12] H. Sponer, Proc. Nat. Acad. Sci. **13**, 100 (1927).

support to this value. Thus 11.8 volts would seem to be a reasonable estimate for D_X. There are, however, several facts which point to a lower value, in the neighborhood of 9.5 volts. The evidence for each of these values will now be considered in a study of the known electron levels of N_2 and N_2^+. These levels, with the configuration class of each, are listed in Table I, together with their probable D values and dissociation products according to each of the two assumptions (1) $D_X = 11.8$ volts, (2) $D_X = 9.5$ volts. In connection with this discussion, the writer is greatly indebted to Professor Birge for information, suggestions, and criticism. Independently of the writer, Birge has also concluded that $D_X = 9.5$ is probably correct.

TABLE I. N_2 *and* N_2^+ *levels and possible dissociation products.*

Level	Probable electron configuration	Electron energy	D(obs.)	D(calc. 1)	D(calc. 1) $-D$(obs.)	D(calc. 2)	D(calc. 2) $-D$(obs.)
$X = {}^1S$	$s^{10}p^4$	0	11.75	$11.8({}^4S+{}^4S)$	+0.0	$9.5({}^4S+{}^4S)$	−2.2
$A = {}^3D$ or ${}^3S$	$s^{10}p^4$	8.2	11.9 (>10.3)	$11.8({}^4S+{}^4S)$	−0.1	11.9 $({}^4S+{}^2D)$	−0.0
$a = {}^1P$	s^9p^5	8.5	14.24 (>10.1)	$16.6({}^2D+{}^2D)$	+2.4	14.3 $({}^2D+{}^2D)$	+0.1
$B = {}^3P$	s^9p^5	9.35	14.6 (>12.9)	$14.2({}^4S+{}^2D)$	−0.4	14.3 $({}^2D+{}^2D)$	−0.3
$C = {}^3P$	s^9p^5	13.0	14.6 (>13.94)	$16.6({}^2D+{}^2D)$	+2.0	$15.45({}^2D+{}^2P?)$	+0.85
$D = {}^3D$ or ${}^3S$	$s^{10}p^4$?	14.8	>14.8	—	—	$16.6?({}^2P?+{}^2P)$	—
$X' = {}^2S$	s^9p^4	16.9	26.0	$23.7({}^2D+{}^2P)$ or $26.3({}^4S+{}^2P)$	−2.7 or −0.3	$26.4({}^2D+{}^2P)$	−0.4
${}^2P$	$s^{10}p^2$	17?	—	$26.3({}^4S+{}^2P)$	—	$24.0({}^4S+{}^2P)$	—
$A' = {}^2S$	s^9p^4	20.1	23.6	$28.7({}^2D+{}^2P)$ or $26.3({}^4S+{}^2P)$	−5.1 or −2.7	$24.0({}^4S+{}^2P)$	−0.4
${}^2S$?	s^9p^4	24	>24	$28.7({}^2D+{}^2P)$	See below	$26.4({}^2D+{}^2P)$, or higher	See below

Notes (*a*) The electronic energies (E) and "observed" D values are all referred to the normal state of N_2 as a zero of energy. Further details, and additional states, will be found in Table III of I (cf. also ref. 61 of I). The "observed" D values ($D = E + D''$) are those given by Birge and Sponer,[7,12,13] or (N_2^+) by Herzberg.[11] The parenthetical inequalities given in the D(obs.) column set extreme lower limits for the correct values of D; the value given in each case (e.g. 10.3 for state A) is the energy value for the highest yet observed vibrational state of the electron level in question. (*b*) In the fifth column the calculated heats of dissociation and probable dissociation products are given on the assumption $D_X = 11.8$, and the observed and calculated D values are compared in the sixth column. In the seventh and eighth columns, a similar correlation and comparison is given for the assumption $D_X = 9.5$. In calculating D values for dissociations giving ${}^2D$ or ${}^2P$ atoms, the value 2.39 volts is used for the energy (above ${}^4S$) of the ${}^2D$ state, and 3.56 volts for that of the ${}^2P$ state.[14] (*c*) The D(calc.) values for N_2^+ make use of the value 14.5 volts for the ionization potential I_a of the unexcited (${}^4S$) N atom;[14] $D(\text{calc.}) = D_X + I_a$ for dissociation into $N^+({}^3P) + N({}^4S)$, or $D_X + I_a + 2.39$ when dissociation yields $N^+({}^3P) + N({}^2D)$.

Let us first consider levels X and A. Two unexcited (${}^4S$) nitrogen atoms (each ${}^4S^S$, s^5p^2) should give four states of N_2, namely a ${}^1S$, a ${}^3S$, a ${}^5S$, and a ${}^7S$ state, all belonging to the $s^{10}p^4$ configuration class. We may identify the normal, ${}^1S$, state X of N_2 with the predicted ${}^1S$ state, and if $D_X = 11.8$, we may identify the lowest excited state A with the predicted ${}^3S$ state. In agreement with this, both these molecular states have $s^{10}p^4$ configurations, and extrapolated D values which are nearly equal. The metastability of state A (cf. I, p. 216) also supports this identification. Heitler has recently reached similar conclusions,[15] showing that $N({}^4S) + N({}^4S)$ should yield two

[13] The observed D value given for state a is a revised recent value of Birge (private communication).

[14] According to Hopfield (Phys. Rev. **27**, 801, 1926), the two largest term values for the neutral nitrogen atom are at 14.49 and 12.10 volts; these are presumably ${}^4S$ and ${}^2D$ respectively in accordance with the Hund theory; hence 2.39 volts probably represents the energy of ${}^2D$. The probable value 3.56 volts for ${}^2P$ is a result of unpublished work of Compton and Boyce (private communication).

[15] W. Heitler, Zeits. f. Physik **47**, 857 (1928).

states (^1S and ^3S) of N_2,—the upper one metastable,—with D^V values similar to those observed for states X and A. The other two (^5S and ^7S) states, Heitler shows, should correspond to states of "repulsion" (i.e., r_0 very large, D^V very small).

If we assume $D_X=9.5$, instead of 11.8, no change is needed in the interpretation of state X; the discrepancy between Birge and Sponer's extrapolated $D_X=11.75$ and the assumed $D_X=9.5$ is, however, surprisingly large; but the extrapolation is a very long one here. With $D_X=9.5$ for state X, we can no longer assume dissociation of state A into unexcited N atoms, since we are sure $D>10.3$ for state A (cf. Table I); the best assumption now is that A is an $s^{10}p^4$, ^3D_z state which gives $^4S+^2D$ on dissociation. A ^3D_z state is to be expected (cf. Tables I and III of I) from the same electron configuration which gives a ^3S state of the kind assumed for state A in the preceding paragraphs; the as yet incompletely known structure of the first positive nitrogen bands ($B\rightarrow A$) appears to be compatible with either a $^3P\rightarrow{}^3S$ or a $^3P\rightarrow{}^3D_z$ transition. Also, such a ^3D_z state should be metastable like the ^3S state.

An argument in favor of the identification of state A with ^3S of $N(^4S)+N(^4S)$, in agreement with $D_X=11.8$, is that if we do not do this, it seems necessary to postulate the existence of an as yet undiscovered additional $s^{10}p^4$ state of this kind; and if such an additional state exists, it is surprising that it does not combine, to give visible or ultra-violet bands, with one of the known states B or C.

Thus for states X and A of N_2, the weight of evidence and plausibility favors $D_X=11.8$. Turning now, however, to state a, we find evidence which strongly favors $D_X=9.5$. From the fact that the N_2 bands $a\leftrightarrow X$ are of high intensity and apparently simple structure, it seems extremely probable that state a is a singlet state; if so, it is necessarily (because of the selection rule for σ_l) either ^1S or ^1P, since X is ^1S. Birge has assumed it to be ^1P, in analogy with CO. Now except for the one ^1S state from $^4S+^4S$ which we have identified with X of N_2, *all* singlet states of N_2 are necessarily derived from *two excited atoms*,—as can be seen from a study of Table II of I. Of ^1P states of N_2, two s^9p^5 states should be obtained from $N(^2D)+N(^2D)$, one s^9p^5 state from $^2D+^2P$, and one $s^{11}p^3$ state from $^2P+^2P$. State a of N_2 should then probably be correlated with $^2D+^2D$ (this would also be reasonable even if a is a ^1S state). As will be seen from Table I, the calculated and observed D values are then in good agreement for state a if $D_X=9.5$ is assumed, but the observed D is too low, by an amount probably exceeding any possible error in the extrapolation, if $D_X=11.8$. This is strong evidence for $D_X=9.5$.

According to Table III of I, the ^3P states B and C of N_2 both have s^9p^5 configurations. By means of Table II of I we find that one s^9p^5, ^3P state should be obtained from $^4S+^2D$, two from $^2D+^2D$, and one from $^2D+^2P$. The most likely correlations for each of the two assumptions $D_X=9.5$ and 11.8 are given in Table I. The agreements are better for $D_X=9.5$.

Data on N_2^+ afford strong evidence for $D_X=9.5$. On the basis of Herzberg's recent revision[11] of the observed D^V values for the 17 and 20 volt

^2S levels of N_2^+ (cf. discussion of N_2^+, above), there appears to be no way of getting reasonable agreement between D (obs.) and D (calc.) for both these states, except to assume $D_X = 9.5$ and at the same time to assume that the dissociation products are $N_2^+(17) \rightarrow N^+(^3P) + N(^2D)$ and $N_2^+(20) \rightarrow N^+(^3P) + N(^4S)$. The justification for this statement will be evident from an examination of the observed D values as compared in Table I with D values calculated for various assumptions.

Besides the 17 and 20 volt ^2S states of N_2^+ there is another, probably also ^2S, level at 24 volts, which is unstable on collision (Smyth, Hogness and Lunn[16]; cf. I, Table III and p. 208). This state of N_2^+ must on *adiabatic* dissociation give at least one excited particle, since the ^2S from unexcited $N^+ + N$ is already accounted for. The possibility of lowest energy is $N^+(^3P) + N(^2D)$. This makes D at least 26.4 or 28.7 volts (according as $D_X = 9.5$ or 11.8) for this state.[11] But Hogness and Lunn in their positive ray experiments have shown that 24-volt N_2^+ is completely dissociated by *collisions* if sufficient opportunity for these is given (high pressure). From this we must conclude either that the ions acquire additional kinetic energy, to the extent of 2 or 4 volts, before colliding, or else that 24 volts is enough energy for dissociation. But Hogness and Lunn explicitly mention the first alternative and give evidence that possession of kinetic energy does *not* promote dissociation of 24 volt N_2^+ (ref. 16, bottom p. 790). The most reasonable explanation seems then to be the following: the collisions which produce dissociation are "collisions of the second kind" in which the energy, although inadequate for *adiabatic* dissociation to $N^+(^3P) + N(^2D)$, becomes available for dissociation into $^3P + ^4S$. But even this process, unless the ions acquire kinetic energy contrary to Hogness and Lunn's conclusions, would require 26.3 volts if $D_X = 11.8$; if $D_X = 9.5$, however, the required energy is reduced to 24.0 volts (cf. Table I), a value which is consistent with the observed dissociation of 24 volt N_2^+ ions on collision. Thus we have another argument in favor of $D_X = 9.5$ volts for N_2.—Incidentally, the value 24.0, after subtraction of the ionization potential of N_2 (16.9 volts) gives a new value $D_X = 7.1$ volts for N_2^+, as compared with Birge and Sponer's value of 9 volts.

The fact that the energy transferred by active nitrogen to other molecules is usually limited to about 9.4 volts (cf. I, discussion and ref. 64) also tends to support $D_X = 9.5$, since active nitrogen is probably atomic nitrogen mixed with products formed by the union of the N atoms.[17]—An argument in favor of $D_X = 11.8$ rather than 9.5 for N_2 is the fact that the high value $D_X = 11.2$ is well assured for the chemically less stable molecule CO.—On the whole, the evidence appears strongly to favor $D_X = 9.5$ volts for N_2, but it is not yet conclusive.[17a]

Carbon monoxide. From the application of his σ_l and s addition rules to CO, Hund has tentatively concluded that the states X, A, B, a and b of CO should all be derived from two normal atoms. This conclusion seems

[16] Hogness and Lunn, cf. ref. 39 of I.

[17] J. Kaplan and G. Cario, Nature, June 9, 1928.

[17a] For additional evidence in favor of $D_X = 9.5$, cf. E. Gaviola, Nature **122**, 313 (1928).

to be in the main verified by the experimental D values (cf. Table III of I). The correlation of atomic and molecular states is quite different than for N_2, in spite of the marked analogies between the molecular levels of CO and N_2.—Let us now consider in detail the correlation of C+O with CO.

Two unexcited atoms, $C(^3P)+O(^3P)$, should give the following molecular states: s^1p^3, ^5P, ^3P, ^1P; s^2p^4, ^5D, ^3D, ^1D, ^5S, ^3S, ^1S, ^5S, ^3S, ^1S, ^5S, ^3S, ^1S; s^3p^5, ^5P, ^3P, ^1P. The s^2p^4 states X and a' (^1S and ^3S?) of CO may probably be identified with two of the above group of states, and the s^3p^5 states a and A (^3P and ^1P) with two more of this group; the experimental D values are about equal for all four of these states, as they should be if this identification is correct. The extrapolated value $D_X = 11.2$ volts is apparently not far wrong in this case, especially since it is confirmed[7] by the value 10.8 obtained from chemical data, assuming only the (probably reliable) value $D_X = 7.0$ for O_2. It is probable that the s^2p^4, ^3S state b also dissociates into normal atoms: only one b vibrational state ($n=0$) is known with certainty, thus indicating a very low value of D^v.[18] It may be that the s^2p^4, ^1S state B also dissociates into normal atoms, although the experimental D value (based on Birge, Int. Crit. Tables, from work of Hopfield and Birge[19]) is too large.

The more highly excited states of CO beginning with state C *must* give at least one excited atom on dissociation, since the electronic energy *alone* now exceeds the heat of dissociation into normal atoms. In the case of *singlet* states of CO not formed from the normal atoms, *both* atoms must be in excited states on dissociation (cf. Table II of I).

Some general considerations on predicted and observed levels. Although eighteen different molecular states are predicted as capable of being formed by the union of two unexcited atoms (C+O), not more than five have as yet been identified. Probably many or most of the remaining states correspond, like the 2^3S state of H_2 formed from two normal H atoms (cf. section in I on Heitler and London's work) and like the ^5S and ^7S states of N_2 formed from two normal N atoms (cf. above), to very unstable molecules, i.e., molecules whose r_0 is very large and D^v very small because of a rapid increase in promotion energy with decreasing r. This must especially be true of such states as ^5D, ^5P, ^5S, since a quintet state ($s=2$) requires the presence of at least four electrons in shells which are not closed, and therefore, as compared with the normal state of CO, requires the excitation of at least two electrons from two different closed shells. If r_0 for such states had values comparable with those of the observed states of CO, the excitation energy for such a process would probably be at least 18 or 20 volts, which would be incompatible with dissociation into normal atoms ($D=11$ volts).

It is possible however, that at least a few comparatively stable excited states of CO capable of dissociating into unexcited atoms remain to be discovered; among the likely possibilities are s^2p^4, ^3D and ^1D, and perhaps s^1p^3, ^3P. It is not unlikely that the hitherto unassigned "triplet carbon bands,"

[18] Cf. R. T. Birge, Phys. Rev. **28**, 1173 (1926); third positive carbon bands ($b \rightarrow a$); also the fact (Birge, private communication), that only the $0 \rightarrow 0$ band is known for $X \rightarrow b$.

[19] Cf. ref. 37 of I.

with $\omega_0' = 1105$, $\omega_0'' = (1714)$, and $\Delta v \sim 160$ (Birge, private communication) are $^3S \rightarrow {}^3P$ or $^3P \rightarrow {}^3S$ and involve an $s^1 1p^3$, ^3P_i state of CO, perhaps the expected state which should dissociate into normal atoms.

Considerations similar to those just given for CO, bearing on the question of observed and predicted states, also apply to the other molecules treated in this paper. In the case of most of them, many reasonably stable excited levels probably remain to be discovered.

Nitric oxide (NO). For the normal, $s^{10}p^5$, ^2P, state of NO, the "observed" D (6.8 volts[19a]) may be compared with the more reliable value calculated indirectly making use of chemical data and D_X values of N_2 and O_2; this indirect value, here recalculated, is $D_X = 7.3$, or 8.4, according as $D_X = 9.5$, or 11.8, for N_2; the observed value 6.8 evidently agrees better with the calculated value 7.3 and so supports $D_X = 9.5$ for N_2. Dissociation into unexcited atoms is in harmony with the theory, since $N(^4S) + O(^3P)$ should give $s^{11}p^4$, ^6S, ^4S, ^2S, and $s^{10}p^5$, ^6P, ^4P, ^2P, the last of these being here identified with unexcited NO. The first excited, ^2S, state of NO has already been discussed in the section on NO in I, and shown to involve a *highly* excited N or O atom. Since unexcited N+O should give only one ^2P state, according to Table II of I, and since this is already accounted for, we must conclude that the *excited* $s^{10}p^5$, ^2P state of NO dissociates to give at least one excited atom. The union of $N(^2D)$ and $O(^3P)$ is capable of giving an $s^{10}p^5$, ^2P state; D for this, assuming $D_X = 9.5$ for N_2, should be $7.3 + 2.4 = 9.7$ volts, in agreement with the observed (but very uncertain) extrapolated $D = 10$ volts. The two remaining known excited states of NO probably correspond to moderately excited atoms, but the data are incomplete.

We next consider NO^+. The molecular states formed by union of unexcited $N(^4S) + O^+(^4S)$ should be ^7S, ^5S, ^3S, ^1S, $s^{10}p^4$, as in the case of $N(^4S) + N(^4S)$; unexcited $N^+(^3P) + O(^3P)$ should give a variety of states like those of $C(^3P) + O(^3P)$. Unexcited NO^+ may reasonably be correlated with ^1S of $N(^4S) + O^+(^4S)$, or perhaps with $N^+(^3P) + O(^3P)$. Assuming $N + O^+$, and using $D_X = 7.3$ for NO, we can calculate D_X for NO^+: $D_X^+ = D_X + I_a - I_m = 7.3 + 13.6 - 9.4 = 11.2$ volts. If the dissociation products are $N^+ + O$, $D_X = 7.3 + 14.5 - 9.4 = 12.4$ volts.

As already pointed out in the section on NO in I, each of Hogness and Lunn's potentials, 21 volts ($N + O^+$) and 22 volts ($N^+ + O$), agrees closely with the calculated D value for ionization and dissociation of NO into the respective unexcited atom and ion.[20] The 21 volt state, being correlated with $N(^4S) + O^+(^4S)$, must then be an S state. Probably it is a ^3S state analogous to the lowest ^3S state of N_2 (i.e., to state A, if $D_X = 11.8$); or, if

[19a] F. A. Jenkins, H. A. Barton, and R. S. Mulliken, Phys. Rev. **30**, 172 (1927).

[20] At each of the potentials 21 and 22 volts, a large fraction of the NO molecules is dissociated directly, according to the data of Hogness and Lunn, while the remainder give NO^+ molecules capable of being dissociated in subsequent collisions.[21] As interpreted by Birge and Sponer,[7] this means that there is a large probability, but not a certainty, that the impinging electron will give the molecule enough vibrational energy to cause dissociation, in addition to the energy of removal of an electron. The observed potentials then probably include, strictly speaking, 1 or 2 volts of vibrational energy.

the normal state of NO^+ gives $N^+ + O$ on dissociation, the 21 volt state may be a ^1S corresponding to X of N_2. The 22 volt state may reasonably be identified with an s^9p^5, ^3P or ^1P state derived from $N^+(^3P)+O(^3P)$, like state a or A of CO. The three ionization potentials of NO then correspond (cf. Table III of I) respectively to removal of a $3p^\pi$, a $2p^\pi$, and a $3s^\sigma$ electron from neutral NO.[22]

Oxygen. Two unexcited (^3P) O atoms should give the following states of O_2 (cf. Table II of I): $s^{10}p^6$, ^5D, ^3D, ^1D, ^5S, ^3S, ^1S, ^5S, ^3S, ^1S; $s^{11}p^5$, ^5P, ^3P, ^1P, ^5P, ^3P, ^1P; $s^{12}p^4$, ^5S, ^3S, ^1S. The two $s^{10}p^6$, ^3S states of Table II, both of which probably dissociate into normal atoms,[7] may evidently be identified with the two predicted $s^{10}p^6$, ^3S states. The 1.6 volt state of O_2, which is a ^1S state according to recent work of the writer,[22a] may correspond to one of the other $s^{10}p^6$ states.

The two $s^{10}p^5$, ^2P states involved in the ultra-violet O_2^+ bands are supposedly analogous (cf. I) to the two states involved in the B bands of NO. The same might then be expected of their dissociation products; that is to say (cf. NO, above), we might expect the lower ^2P to dissociate into unexcited $O^+ + O$ ($^4S+^3P$) and the upper ^2P into $O^+(^2D)+O(^3P)$. (Other excited states of O^+ or O are of course not entirely excluded as possible dissociation products.) Or perhaps, unlike NO, the excited ^2P might give unexcited $O^+ + O$, and vice versa. As a matter of fact, as we shall see, the empirical data indicate dissociation into unexcited $O^+ + O$ for *both* ^2P states; the evidence is strong in the case of the lower state, and practically conclusive for the upper state. But since this is quite impossible according to the theory (cf. NO, above), we must apparently conclude that this evidence is unreliable for one of the two states, in all probability the lower, since it is weaker there. We have then probably a reversal of energy order during molecule formation, as in the case of N_2^+ discussed above.

For the process $O_2 \rightarrow O^+(^4S)+O(^3P)$, the total energy D' can be calculated from the known D_X of O_2 and the ionization potential I_a of the O atom: $D' = D_X + I_a = 7.02 + 13.56 = 20.58$ volts. For $O_2 \rightarrow O^+(^2D)+O(^3P)$, the total energy is 3.32 volts higher[23]: $D' = 20.58 + 3.32 = 23.9$ volts.

For each of the two ^2P states of O_2^+, D' is known empirically as the sum of the three quantities I_m (ionization potential of O_2), E^e (electronic energy above the normal ^2P state), and D^v. For the upper ^2P level, the value $D^v = 1.76$ volts is known from Birge and Sponer's work, and is probably reliable within a few tenths of a volt. For the lower ^2P level, the value of D^v depends on the uncertainly known value of E^e of the upper level; assuming $E^e = 5.2$ volts, Birge and Sponer's method gives $D^v = 6.9$ volts. Assuming $I_m = 13.5$ (this, like E^e, is uncertain within a volt—cf. I), we find for the lower ^2P

[21] Cf. note 43 of I.

[22] For the 21 volt potential at least, the possibility is excluded that it is a $2s^\sigma$ or a $3s^\sigma$ electron which is removed, since such removal would give a P state of the molecule, which would be incompatible with $N(^4S)+O^+(^4S)$.

[22a] R. S. Mulliken, Phys. Rev., Dec., 1928: interpretation of atmospheric oxygen bands.

[23] 3.32 volts is the energy required to excite O^+ from ^4S to ^2D: cf. I. S. Bowen, Phys. Rev. **29**, 231 (1927); H. N. Russell, Phys. Rev. **31**, 27 (1928).

state, $D'=13.5+0+6.9=20.4$ volts, and for the upper ^2P state, $D'=13.5+5.2+1.8=20.5$ volts. Both agree well with the calculated value 20.58 volts for dissociation into unexcited atoms. For the upper state, the value of D' is also supported by independent evidence, for as shown in I (p. 212), Hogness and Lunn's ionization potential at 20 volts, at which simultaneous dissociation and ionization occur, in all probability corresponds to the convergence limit of the vibrational levels of the upper ^2P state.[24] Because of this evidence, and in view of the much longer extrapolation involved for D^v in the lower than in the upper state, the value of D' is clearly more probably reliable for the upper than for the lower state. We therefore accept the agreement of the observed and calculated D' for the upper state and so conclude that this state dissociates into unexcited $O^+ + O$, but reject on theoretical grounds (cf. above) the agreement for the lower state—in spite of the fact that the discrepancy between the theoretical value $D'=23.9$ which we must now assign to it and the empirical $D'=20.4$ is unaccountably large. —As a possible escape from this discrepancy, it is of course true that errors may exist in the classification of the O_2^+ levels, since our knowledge of the O_2^+ bands is very incomplete (cf. I).

Fluorine. For two fluorine atoms, we need consider only the normal state of each; there are no excited states of low energy. Two such atoms should give: s^2p^6, ^3D, ^1D, ^3S, ^1S, ^3S, ^1S; s^2p^5, ^3P, ^1P, ^3P, ^1P; s^2p^4, ^3S, ^1S. The two observed ^1S, s^2p^4 states, both of which dissociate into normal atoms,[25] must probably be correlated with the two expected ^1S, s^2p^6 states, in spite of the fact that this involves a violation of the $\sigma_l\tau$ conservation rule.[26]

General conclusions. With two possible exceptions (state a of N_2, if $D_X=11.8$, and one state of O_2^+), all the assignments made in Table III of I are in conformity with Hund's rule that σ_l and s for the molecule should be obtained from the atomic σ_l and s values by addition. A further conclusion is that, with the exception of the two states of F_2 and possibly also of the two states (of N_2 and O_2^+) just mentioned, no contradiction is found to the applicability of the (non-detailed) $\sigma_l\tau$ conservation rule during molecule formation. This empirical result is especially valuable because no strict theoretical basis has been obtained for the rule.

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[24] Recent work of Smyth and Stückelberg (Phys. Rev. **32**, 779 (1928) gives new evidence, in agreement with Hogness and Lunn's results, that $O^+ + O$ is formed by electron impact at 20 volts.

[25] The normal ^1S state of F_2, judging by analogy with Cl_2, Br_2, and I_2, gives $F(^2P_{1\frac{1}{2}}) + F(^2P_{1\frac{1}{2}})$ on dissociation, while the excited ^1S state gives $F(^2P_{1\frac{1}{2}}) + F(^2P_{\frac{1}{2}})$: cf. J. Franck, Trans. Far. Soc. 21, Part 3, 1925, and H. Kuhn, Zeits. f. Physik **39**, 77 (1927). Such differences are, however, unimportant for present purposes, since Δv is small for light atoms. Similar differences must exist in other cases where multiple atomic levels are involved (e.g. ^3P of oxygen).

[26] The possibility that one or both of the observed ^1S states may really be of an s^2p^6 type seems relatively small, in view of the evidence given in I for the configurations there assigned.

THE NEAR INFRA-RED VIBRATION SPECTRUM OF THE CARBONATES

By Harold H. Nielsen

Abstract

An attempt has been made to solve theoretically the problem of the frequencies and intensities of the near infra-red absorption regions of the carbonate group. The assumption, that in the normal state the oxygen nuclei are located at the vertices of an equilateral triangle while the carbon nucleus lies at the center, seems justified by the x-ray investigations of the crystal structure of the group. Using a general potential energy function with three constants under the assumption that the fields of force surrounding the nuclei are central, the normal modes of infinitesimal vibration are determined, yielding four independent frequencies ν_1, ν_2, ν_3, and ν_4, of which ν_4 is optically inactive. Through the three disposable constants, ν_1, ν_2, and ν_3 may be made to coincide with the three fundamental absorption regions found experimentally by Schaefer and Schubert, and it is found that the optically inactive frequency ν_4 agrees closely with the value predicted by Schaefer, Bermuth and Matossi. From a consideration of the change of electric moment, the theoretical intensities are determined. It is found that the relative intensities obtained theoretically agree well with the values determined by Schaefer and Schubert.

IN THE near infra-red absorption spectra of the group of crystals calcite ($CaCO_3$), magnesite ($MgCO_3$), dolomite ($Mg(CO_3)_2Ca$), and others, there are observed three principal regions of absorption at 6.7μ, 11.38μ, and 14.16μ, which may be attributed to the fundamental vibrations of the carbonate radical. Of these the region at 11.38μ has been shown by Schaefer and Schubert[1] to correspond to a vibration along the optical axis of the crystal while the other two correspond to vibrations perpendicular to this axis. In addition to the three principal absorption regions there are a number of weaker absorption peaks which may be interpreted as harmonics and combinations of the fundamental frequencies. An essential point of this interpretation, however, is that besides the three observed fundamentals there must exist a fourth fundamental frequency which lies at about 9.0μ. Since this latter can not be determined directly, but only through combination bands, it is termed optically inactive.

From x-ray analysis of the structure of these carbonates, we learn that the carbonate configuration is an equilateral triangle at whose vertices are located the oxygen particles and at whose center is located the carbon particle. The distance from an oxygen atom to the carbon atom is given by Wycoff as 1.225×10^{-8} cm. The plane of the three oxygen atoms is perpendicular to the optical axis, hence it may be concluded from the work of Schaefer and Schubert that the vibrations corresponding to the regions of absorption at 6.7μ and at 14.16μ lie in the carbonate plane while that at 11.38μ is perpendicular to it.

[1] Cl. Schaefer and M. Schubert, Ann. d. Physik, 50, 283 (1916).

H. Kornfeld[2] has attacked the problem of the vibrations of the carbonate group with considerable success. In order to obtain the potential energy function he has assumed that each oxygen particle is the seat of a double negative charge and that the carbon particle possesses a fourfold positive charge. He has further assumed that the electron configuration that surrounds each oxygen is capable of a polarization. Using the two disposable constants α, the polarization and r, the distance of an oxygen atom from the carbon atom he has been able to correlate his theoretical values for the frequencies with the observed values with an accuracy of from 10 to 15 percent. The value of r which he found was 1.5×10^{-8}, a value somewhat larger than that given by x-ray analysis.

In the light of our present knowledge of the structure of molecules, Kornfeld's model is subject to criticism on the ground that the atoms composing a molecule are probably not completely ionized as he has assumed, but rather that there exists a large perturbation resulting in a more or less mutual sharing of electrons among the atoms. In the present note it is proposed to analyze the motion of the carbonate group by the use of a general potential energy function with three disposable constants.

Certain assumptions must, however, be made with regard to the form of the potential energy function and we shall consider that the forces surrounding each atom are central, believing that the departure from this assumption caused by the presence of polarizations will not in first approximation alter the character of the motion or the fundamental frequencies.

The assumption is made herein that the amplitudes of vibration of the nuclei are small so that the higher order terms of the potential and kinetic energy may be neglected. The system which we are considering is one of twelve degrees of freedom, but since we are chiefly interested in the vibrations we may choose only six mutual coordinates neglecting the translational and rotational motion of the group as a whole. If the displacements of the oxygen atoms with respect to each other are represented by q_1, q_2, q_3; and the displacements of the oxygens with respect to the carbon by q_4, q_5, q_6; then since the forces acting on the nuclei are considered to be central, the potential energy for an arbitrary displacement may be expressed as follows:

$$W=\sum_{i=1}^{3}f(q_i)+\sum_{k=4}^{6}F(q_k) \tag{1}$$

where f and F are unknown functions. W may be developed by Taylor's theorem, and all terms above the second order disregarded.

$$W=W_0+(df/dq_i)_0(q_1+q_2+q_3)+(dF/dq_k)_0(q_4+q_5+q_6)$$
$$+(1/2)(d^2f/dq_i^2)_0(q_1^2+q_2^2+q_3^2)+(1/2)(d^2F/dq_k^2)_0(q_4^2+q_5^2+q_6^2)+\cdots \tag{2}$$

Only three of the four constants that appear in this expression for the potential energy are independent since the equilibrium condition imposes the relation:

[2] H. Kornfeld, Zeits. f. Physik **26**, 205 (1924).

$$(df/dq_i)_0=(1/3^{1/2})(dF/dq_k)_0. \tag{3}$$

It is found convenient for calculation to express the potential energy in slightly different coordinates. The coordinates used are the q_1, q_2, q_3 defined above, and three others, x, y, z, components of a vector R which represents the distance of the carbon particle from the center of gravity of the oxygen nuclei. The kinetic and potential energies for infinitesimal displacements may quite readily be determined under the conditions that the linear and angular momenta of the molecules shall be zero, by letting each coordinate vary independently and then studying the total resultant displacement of each nucleus. Treating the energy expressions in the usual manner to determine the normal modes of vibration, the characteristic determinant,[3] the roots of which determine the frequencies may be written in this case:

$$\left(\frac{3}{\mu}\lambda-\frac{3\cdot 3^{1/2}}{2}\beta\right)\left(\frac{\lambda}{3}-\frac{1}{3}-\alpha\right)\left(\frac{2}{\mu}\lambda^2-\lambda\left[1+\frac{1}{\mu}+\frac{3^{1/2}}{2}\beta\left(1+\frac{1}{\mu}\right)+\frac{3}{\mu}\alpha\right]\right.$$
$$\left.+3^{1/2}\beta+\frac{3\cdot 3^{1/2}}{4}\alpha\beta+\frac{3}{2}\alpha\right)^2=0,$$

where:

$$\alpha=K_1/K_2\ ;\quad \beta=c/K_2\ ;\quad \mu=(M+3m)/M\ ; \tag{4}$$

$$\frac{1}{a}\left(\frac{dF}{dq_k}\right)_0=\frac{c}{2}\ ;\quad \left(\frac{d^2f}{dq_i^2}\right)_0=K_1\ ;\quad \left(\frac{d^2F}{dq_k^2}\right)_0=K_2.$$

and where a is the normal side of the equilateral triangle configuration. The roots of the determinant shall be denoted by λ_1, λ_2, λ_3, and λ_4, where λ_2 and λ_3 are the double roots and where $\lambda_2>\lambda_3$. These give rise to four independent frequencies, ν_1, ν_2, ν_3 and ν_4, where

$$\nu_i=(1/2\pi)(K_2\lambda_i/m)^{1/2}$$

These frequencies are respectively:

$$\nu_1=\frac{1}{2\pi}\left(\frac{K_2}{m}\right)^{1/2}\left[\frac{3^{1/2}\beta\mu}{2}\right]^{1/2}\ ;\quad \nu_4=\frac{1}{2\pi}\left(\frac{K_2}{m}\right)^{1/2}(1+3\alpha)^{1/2}$$

$$\nu_2=\frac{1}{2\pi}\left(\frac{K_2}{m}\right)^{1/2}\left\{\frac{2+3^{1/2}\beta(\mu+1)+6\alpha}{8}+\left[\frac{\mu-1}{2}\left(\frac{1}{2}+\frac{3^{1/2}\beta}{4}\right)+\frac{3\alpha}{4}\right]\right\}^{1/2} \tag{5}$$

$$\nu_3=\frac{1}{2\pi}\left(\frac{K_2}{m}\right)^{1/2}\left\{\frac{2+3^{1/2}\beta(\mu+1)+6\alpha}{8}-\left[\frac{\mu-1}{2}\left(\frac{1}{2}+\frac{3^{1/2}\beta}{4}\right)+\frac{3\alpha}{4}\right]\right\}^{1/2}$$

The system is degenerate since while it has six degrees of vibrational freedom, only four independent frequencies enter into its motion.

[3] E. T. Whittaker, A Treatise on the Analytical Dynamics, 3rd edition, p. 178.

A study of the motion reveals that ν_1 corresponds to a vibration of the carbon nucleus along the axis of symmetry of the model, the distance between the oxygen nuclei remaining unchanged. Since λ_2 and λ_3 are each double roots two arbitrary constants occur in the motion corresponding to ν_2 and ν_3. This corresponds to a motion of the carbon particle in the plane perpendicular to the axis of symmetry, the path being an ellipse subject to the restriction that the sum of the squares of the major and minor axes is a constant. The eccentricity as well as the orientation of the path will depend on the arbitrary constants involved. The frequency ν_4 corresponds to a motion of the oxygen nuclei symmetrical with respect to the axis of symmetry, the carbon remaining fixed at the center of gravity. It should be noted that this latter is the inactive frequency, for unlike the other three vibrations there is here no changing electric moment.

The theoretical frequencies which the model predicts contain three constants α, β, and K_2 which may be determined by using the observed values of the three bands. The experimental work of Schaefer and Schubert shows that the absorption regions at $6.7\mu(447\times10^{11})$ and $14.16\mu(212\times10^{11})$ are due to vibrations of the carbon in the plane of the model. Since $\lambda_2>\lambda_3$ and $\lambda_i\propto\nu_i^2$ we can immediately identify ν_2 and ν_3 with the frequencies 447×10^{11} and 212×10^{11} respectively. The region at $11.38\mu(263.5\times10^{11})$ is evidently due to a vibration of the carbon nucleus perpendicular to the plane of the model since it disappears when the spectrum is observed with the crystal cut perpendicular to the optical axis. Hence we identify ν_1 with the frequency 263.5×10^{11}. The values obtained for these constants are:

$$\alpha=0.263; \qquad \beta=0.248; \qquad K_2=3.064\times10^4.$$

Knowing these values it is now possible to compute theoretically the position of the band corresponding to the inactive frequency ν_4, and we obtain the value 8.98μ which is in good agreement with that predicted by Schaefer and his collaborators.[4]

We now proceed to the computation of the values of the theoretical intensities. It may be shown that the integral of the coefficient of absorption α over an absorption region is associated with the amplitude of the change of the electric moment by the relation:

$$(g_0/g_i)\int \alpha_\nu d\nu = KA^2{}_i\nu_i \tag{6}$$

where A_i denotes the amplitude of the change of the electric moment and where g_0 and g_i are the *a priori* probabilities of the normal and the ith states respectively and where K is a constant independent of ν_i. α_ν is the absorption coefficient which is to be determined experimentally. Following the notation of Dennison[5] we shall let ρ_i^2 equal the left member of (6) and be defined as the experimental intensity, while the right member shall be defined as the theoretical intensity.

[4] Cl. Schaefer, C. Bermuth, and F. Matossi, Zeits. f. Physik **39**, 648 (1926).
[5] D. M. Dennison, Phil. Mag. **1**, 195 (1926).

In accordance with the assumptions made earlier that the forces acting upon the nuclei are central, it is now assumed that each nucleus may be thought of as the seat of an effective charge and hence that the change of electric moment is directly proportional to the displacements of the carbon nucleus with respect to the center of gravity of the oxygen atoms. It is to be expected that this assumption will hold best in comparisons between the intensities of bands corresponding to motions involving the same direction of displacement of the carbon atom, that is between the bands at 6.7μ and 14.16μ, and to hold less well for the 11.38μ band where the carbon vibrates perpendicular to the plane of the oxygens. According to the assumption just stated A_i, the amplitude corresponding to the fundamental band ν_i will be given by the product of the amplitude of the normal coordinate and K_i, a proportionality constant between the displacement of the carbon and the normal coordinate.

$$A_i^2 = hK_i^2/2\pi m\nu_i$$

The theoretical intensities of the active frequencies appear in the fourth column of Table I, where the constant is so chosen that the theoretical and experimental intensities of the band at 6.7μ are in agreement.

TABLE I.

	Frequency (Theo.)	Frequency (Obs.)	Direction of vibration of electric moment relative to line of symmetry	(Theo.) ρ_i^2	(Obs.) ρ_i^2
ν_1	263.4×10^{11}	263.5×10^{11}	$\parallel$	34	17
ν_2	447.0	447.	$\perp$	30	30
ν_3	211.9	212.	$\perp$	4	4
ν_4	334.0	330. (predicted value)	...	0	0

The fifth column of the table contains the experimental intensities as estimated from the reflection curves of Schaefer and Schubert. Due to the extreme intensity of absorption of the fundamental bands in the carbonates, the values for α have never been measured. It may readily be proved, however, that to every maximum of absorption there exists a corresponding maximum of reflection, i.e., where r, the reflection coefficient becomes a maximum. The two maxima do not exactly coincide, the reflection maximum being displaced slightly toward the longer wave-lengths. It may further be shown that for the range of reflections in which we are interested the reflection coefficient r is approximately proportional to the absorption coefficient and hence the observed reflection curves already mentioned may be used for determining the experimental intensities. The *a priori* probabilities g_0 and g_i are all to be taken equal to unity since the measurements of Schaefer and Schubert were made with a crystal cut parallel to the optical axis. No claim is made that the experimental intensities here given are of any great precision, but it is believed that they are of the right order of magnitude.

In conclusion we may say that by using a simplified potential energy function with three disposable constants, it has been possible to correlate three of the four independent frequencies ν_1, ν_2, ν_3, to the three fundamental absorption regions measured experimentally by Schaefer and Schubert, while it has been shown that the fourth, optically inactive frequency ν_4 coincides very closely with the value predicted by Schaefer, Bermuth and Matossi from combination bands. A comparison of the theoretical and experimental intensities has been made resulting in an agreement which we believe to be real and to furnish at least a partial vindication of the simplicity of the method which we have employed.

I wish to utilize this opportunity to express my gratitude to Professor D. M. Dennison at whose suggestion I undertook this problem and who through his many helpful suggestions has aided me in the preparation of this paper.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MICHIGAN,
July 30, 1928.

IONIZATION BY COLLISIONS OF THE SECOND KIND IN MIXTURES OF OXYGEN WITH THE RARE GASES

By H. D. Smyth and E. C. G. Stueckelberg

Abstract

Harnwell's experiments on ionization by collisions of the second kind have been continued. Mixtures of oxygen with argon, neon and helium and incidental effects of water vapor have been studied. Evidence of the following collisions of the second kind was obtained:

(1). $A^+ + O_2 \rightarrow O_2^+ + A$
(2). $A^+ + H_2O \rightarrow H_2O^+ + A$ (very strong)
(3). $H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$
(4). $Ne^+ + O_2 \rightarrow O^+ + O + Ne$
(5). $He^+ + O_2 \rightarrow O^+ + O + He$

The experiments confirm the conclusions of Hogness and Lunn as to the processes of ionization in oxygen but leave the exact value of the first ionizing potential uncertain.

DURING the last year Harnwell[1] published two papers on ionization by collisions of the second kind in mixtures of gases. The present paper describes an extension of his work to include mixtures of oxygen with the rare gases and some incidental effects of water vapor. The object of the work was twofold. In the first place it appeared desirable to study oxygen as a matter of routine so that with Harnwell's results on hydrogen and nitrogen a basis would be laid for experiments on mixtures of these three elementary gases and their compounds. In the second place, there are numerous discrepancies in previous work on oxygen which it was hoped might be cleared up.

A summary of the work on oxygen may be found in Franck and Jordan.[2] Stated briefly the situation is this. The ordinary first ionizing potential of oxygen corresponds to the production of stable O^+_2 but the exact value of the I. P. (ionizing potential) is uncertain, the experimental determinations ranging between 12.6 and 16.1 volts, the values observed by Mackay who was the only observer to find two distinct "breaks" in the ionization curve. There is also a higher I. P. apparently a little above twenty volts which corresponds to a direct production of O^+ ions. Finally there is the spectroscopically determined value of the I. P. of atomic oxygen, 13.6 volts.

It is quite possible, of course, that Mackay was right and that there are two ionizing potentials only a few volts apart and both giving a stable molecular ion. On the other hand, it is now a perfectly familiar idea that molecular ionizing potentials are always difficult to determine exactly experimentally because of the association of vibrational and rotational energy with the electronic energy. There are, therefore, two possibilities with regard to oxygen. First, that there are two ionizing potentials and that all

[1] G. P. Harnwell, Phys. Rev. **29**, 683 and 830 (1927).
[2] Franck and Jordan, Anregung von Quantensprüngen, p. 273.

observers except Mackay have measured an average value. Or second, disregarding Mackay's result, that there is one ionizing potential but its value is uncertain. The first hypothesis seems much the more probable but in either case it was thought that a study of collisions of the second kind in a mixture of oxygen and argon would be interesting since the I. P. of argon is 15.69 as determined spectroscopically. Mixtures with neon were also promising since the I. P. of neon is 21.6 just about the same as that for the production of O^+ ion from diatomic oxygen. Experiments were also done with helium as a matter of routine and some rather striking effects of water vapor were noticed and studied.

Apparatus and Procedure

Experiments were started with the same apparatus which Harnwell had used in the previous year. It seemed, however, to be suffering from age and was unable to give reproducible results. After the loss of a good many weeks a new apparatus was set up. Except for the elimination of one grid and small changes in dimensions it was essentially the same as Harnwell's and it is not necessary to describe it. The procedure was also unchanged. Accelerating fields of forty to sixty volts gave electrons from the filament plenty of energy to produce ions of all kinds in the gas mixture and the relative intensities of the different types of ions were determined by positive-ray analysis and studied as a function of pressure.

Results

It was not found possible to get exactly reproducible quantitative results but by making repeated experiments perfectly definite qualitative results were obtained. Runs were made first with pure oxygen, then with oxygen and argon, then with pure oxygen again and with pure argon. The runs on pure oxygen confirmed Hogness and Lunn's conclusion that the ratio of O_2^+ to O^+ is essentially independent of the pressure, suggesting that

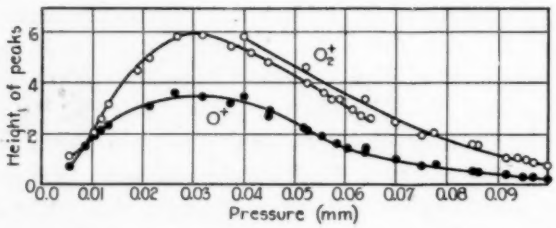

Fig. 1. Pure oxygen. Two overlapping runs. Field accelerating the electrons, $V_1=45$ volts; field to draw out positive ions, $V_2=2$ volts; thermionic current, $i=60$ microamps.

the O^+ is formed directly by electron impact without the need of additional collisions. This is, of course, in contrast to the cases of hydrogen and nitrogen. The relative intensity of O^+ and O_2^+ is much more like that found in

[5] H. D. Smyth, Proc. Roy. Soc. **105A**, 116 (1924).
[6] Hogness and Lunn, Phys. Rev. **27**, 732 (1926).

the early work of Smyth[3] than in Hogness and Lunn's[4] work. Nor is this discrepancy due to impurities as they suggest since both this and the earlier apparatus were capable of resolving N^+, O^+, and H_2O^+.

Pure oxygen. An example of the results in pure oxygen is shown in Fig. 1 where the ordinates are the heights of the "peaks" measured by the electrometer and may be taken as proportional to the numbers of different types of ions coming out of the ionization chamber. The points plotted are from two different runs taken several days apart and over different ranges of pressure. The two runs overlapped in the pressure range from 0.04 to 0.065 mm and the discrepancy between the two sets of points was sufficient in the case of O_2^+ to suggest the drawing of two separate curves. Since the agreement for the O^+ points was much better only one curve was drawn. The general shape and relationship of these two curves was perfectly reproducible but the absolute values of the ordinates were not. The values of thermionic current, voltage, etc., for these runs and later ones are given in the captions of the figures.

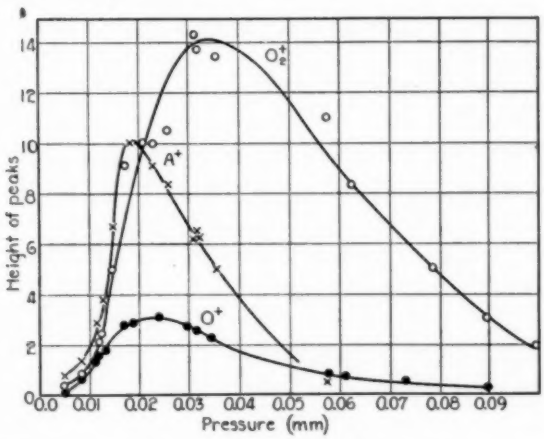

Fig. 2. Equal parts (by volume) of oxygen and argon. $V_1=41$; $V_2=2$; $i=60$.

Argon and oxygen. The striking feature of the runs on argon and oxygen is the increase of the ratio of O_2^+ to O^+ ions. This is illustrated by the curves shown in Fig. 2 and is interpreted as evidence of collisions of the second kind of the following type,

$$A^+ + O_2 \rightarrow O_2^+ + A \qquad (1)$$

In attempting to get a run on pure argon the utmost difficulty was experienced in getting rid of water-vapor ions. When a blank run or one with oxygen or a mixture showed no trace of H_2O^+ a run with the most carefully dried argon gave quantities of it, increasing very strongly with increased pressures. Prolonged baking out of connecting tubing, etc., reduced it but never eliminated it entirely. The curves in Fig. 3 give an example of the situation after drastic attempts at drying. The smallest intensity obtained was roughly one-half of that shown. This continued presence of H_2O^+ ions is interpreted as evidence of the occurrence of the reaction,

$$A^+ + H_2O \rightarrow A + H_2O^+ \qquad (2)$$

Furthermore, the smallness of the water "peak" in oxygen even when it was intentionally wet suggests the likelihood of the reaction,

$$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O \qquad (3)$$

It was difficult to estimate the amount of water vapor in the tube but it was certainly very small. Speaking qualitatively it appears that the reaction (2) is very probable indeed, more so than any other electron transfer observed either here or in Harnwell's work while (1) is fairly probable and we have no way of estimating the probability of (3).

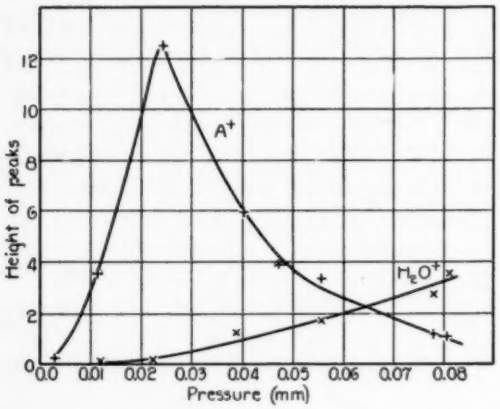

Fig. 3. Carefully dried argon. $V_1=45$; $V_2=2$; $i=60$.

Now the I. P. of water has been determined experimentally three times or more and appears to be definitely within 0.5 volt of 13.0 volts.[5] The difference between this and 15.67 appears too large to account for the strength of the reaction (2) and suggests either that there is another I. P. for H_2O corresponding to the removal of a different electron or that the ionization by a collision of the second kind is accompanied by excitation to a higher vibration state than results from ionization by electron impact. This last hypothesis seems more likely but our knowledge of energy levels is insufficient to test it in this or analogous cases.

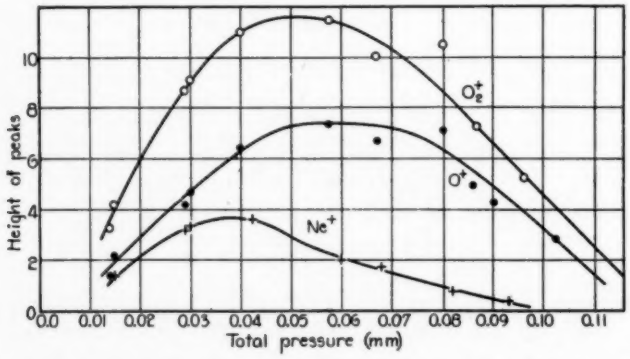

Fig. 4. Equal parts (by volume) of oxygen and neon. $V_1=50$; $V_2=2$; $i=60$.

As to the I. P. of oxygen we can say definitely that it is below that of argon. Judging from the probability of reaction (1) we should say considerably below, perhaps even less than 13 volts which would mean that

[5] Barton and Bartlett, Phys. Rev. **31**, 822 (1928)

that same I. P. was involved in (3) as in (1). This would agree with the results of Hogness and Lunn rather than with those of Smyth and others. However, we cannot be certain that there are not two I. P.'s in this region. Attempts to make critical potential runs with the present apparatus were rather unsatisfactory although they showed that the different types of ions appear in the expected order, first O_2^+ then A^+ and finally O^+.

Neon and oxygen. Since the I. P. of neon is known to be 21.6 volts, very near to that for O^+ it was thought mixing in neon might have a marked effect on the intensity of O^+. That this was the case is evident from Fig. 4 which shows the relative intensity of O^+ very much enhanced. This is interpreted as the result of the reaction

$$Ne^+ + O_2 \rightarrow Ne + O + O^+ \qquad (4)$$

which appears to be quite probable.

In the mixtures of neon and oxygen a curious effect was noticed. After oxygen had been in the tube it was found very difficult to get any neon ions, apparently because the electrons never got sufficient velocity to ionize neon. This was in spite of the fact that the applied voltage was more than twice the I. P. It was thought that the violent measures used in trying to get rid of water vapor in the experiments on argon might have distilled some grease from one of the liquid air traps on to the platinum grid in the ionization tube and that a charged layer was being formed. Taking the apparatus down and cleaning it reduced the effect considerably but did not eliminate it. Critical potential runs still showed the peculiar result of approximately correct I. P.'s for oxygen but values 10 to 15 volts too high for neon. Check experiments with argon showed no such effect but it was quite strong in helium. The experiments on which the conclusions as to reaction (4) are based were taken with high (about 50 volts) accelerating potential and there is no reason to suppose that they are at all invalidated by this "layer" effect. It remains as an observation probably of no real importance but not entirely explicable.

Helium and oxygen. The experiments with mixtures of helium and oxygen showed the expected result, that is evidence of the occurrence of the reaction,

$$He^+ + O_2 \rightarrow He + O + O^+ \qquad (5)$$

but with smaller probability than (4).

Conclusion

These experiments have confirmed previous conclusions as to the processes of ionization in oxygen and the transfer of electrons by collisions of the second kind. They have brought to light the high probability of the ionization of water vapor by argon ions. But they have not had much success in solving the problem of the correct value or values of the I. P. of oxygen.

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July 23, 1928.

THE IONIZATION PROCESSES OF IODINE INTERPRETED BY THE MASS-SPECTROGRAPH

By T. R. Hogness and R. W. Harkness

Abstract

Positive ions produced in iodine by electron impact.—With an apparatus previously described in which positive ions, formed by electrons of definite energy are accelerated and then deflected magnetically around a semicircle into a Faraday cylinder, the relative numbers of the ions I^+, I_2^+, and I_3^+ were measured as a *function of pressure* from 2×10^{-5} to 4×10^{-3} mm. In the primary process of electron collision, I^+ and I_2^+ were both formed. I_3^+ was also formed in secondary collision from I^+ by the process $I^+ + I_2 = I_2^+ + I$ and I_3^+ was formed from I_2^+ by the process $I_2^+ + I_2 = I_3^+ + I$. Evidence and argument against other possibilities are given. The disappearing potentials of I^+ and I_2^+ were found to be identical, 9.3 volts.

Negative ions formed from iodine gas and free electrons.—Three negative ions I^-, I_2^-, and I_3^- were found to exist in quantities comparable with those of positive ions. Pressure-intensity relationships of these ions were also determined. I^- is formed both near the filament and in the ionization chamber according to the equation $I_2 + E^- = I^- + I$. I_2^- and I_3^- are not formed by collision with free electrons but as a result of secondary collisions of I^- and I_2^-, respectively, with I_2 molecules: $I^- + I_2 = I_2^- + I$; $I_2^- + I_2 = I_3^- + I$.

THE amount of spectroscopic and critical potential information concerning the halogens, acquired during the last few years, has made a study of the ionization processes occuring in these gases very desirable, but because of the relatively great reactivity of these elements such a study has thus far been postponed. Studies of all these elements may be impossible but knowledge of the ionization processes occurring with any one of them can, perhaps, be applied generally to the others. Iodine was selected for this investigation, offering perhaps less experimental difficulty than will the other members of this group and being that element about which we have the most information.

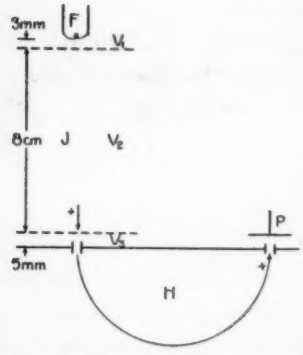

Fig. 1. Schematic arrangement of the fields.

A new apparatus was constructed for this work. In principle, it was the same as that employed by Hogness and Lunn, Smyth and others[1] differing in detail from that of Hogness and Lunn in that larger pole pieces and greater field strengths were used, thereby giving greater resolution for ions of greater mass. The radius of curvature of the ion path was 7 cm instead of 5 cm formerly used, and a field strength of 20,000 gauss was possible; 16,000 gauss, the maxmum used in this investi-

[1] For references, see Smyth, Phys. Rev. **25**, 452 (1925), Hogness and Lunn, Phys. Rev. **30**, 26 (1927). Barton and Bartlett, Phys. Rev. **31**, 822 (1928). Kallman and Bredig, Zeits. f. Physik **34**, 736 (1925).

gation, made it possible to determine a mass of 381 with about 1 percent accuracy.

In discussing the present work, it will be occasionally necessary to refer to the various electrical fields employed. To facilitate the discussions, a schematic arrangement of the fields is given in the accompanying figure. The diagram indicates the distances between the various gauzes and the path of the positive ions. When negative ions were studied, V_2, V_3 and the polarity of the magnetic field were reversed. Electrons from the filament F enter the ionization chamber J and here produce ions of the gas. The various ions formed here follow the path indicated in the diagram. The magnetic field in the region H is kept constant and the e/m value for each ion is determined by the value of the voltage in the field through which the ion falls, according to the relationship

$$e/m = 2V/H^2r^2$$

where V is the applied voltage, H the magnetic field strength and r the radius of the circle which the ion follows in the magnetic field

Positive Ions

The following processes represent the mechanism of the principal reactions producing the positive ions, I^+, I_2^+ and I_3^+:

Primary processes:

(1) $I_2 = I_2^+ + E^-$

(2) $I_2 = I^+ + I + E^-$

Secondary processes:

(3) $I^+ + I_2 = I_2^+ + I$

(4) $I_2^+ + I_2 = I_3^+ + I$

The method of distinguishing between primary and secondary processes was the usual one of determining the dependence of the relative intensities of the various ions upon pressure. Four different pressures were employed, 4×10^{-3}, 7×10^{-4}, 1×10^{-4} and 2×10^{-5}, a pressure variation of 200 fold. These pressures are the equilibrium pressures of the vapor over solid iodine at $-18.5°$, $-33°$, $-45°$, and $-55°$C, respectively. The iodine was contained in a large tube immediately adjoining the ionization chamber. The variations of the relative intensities of the four ions I^+, I_2^+, I_3^+, and I^{++} are shown in Table 1. Each determination is the mean of several.

Table I. *Variation of the relative intensities of the ions* I^+, I_2^+, I_3^+, *and* I^{++}.

Pressure in mm	2×10^{-5}	1×10^{-4}	7×10^{-4}	4×10^{-3}
$\frac{\text{Intensity of } I_2^+}{\text{Intensity of } I^+}$	0.6	1.3	16	32
$\frac{\text{Intensity of } I_3^+}{\text{Intensity of } I^+}$	—	Very small	0.26	2.5
$\frac{\text{Intensity of } I^{++}}{\text{Intensity of } I^+}$	—	0.07	0.05	0.15

The first intensity ratio against pressure given in the table indicates that the formation of I_2^+ is a secondary process involving the comsumption of

I^+, formed by a primary act, but if I_2^+ were formed only by a secondary process, then the intensity ratio of I_2^+ to I^+ should fall practically to zero at the lowest pressure. The fact that at this very low pressure the intensities of I_2^+ and I^+ are of the same order of magnitude indicates that I_2^+ is also formed by a primary process (Eq. 1). The mean free path of the ions at this lowest pressure is so large as to preclude the possibility of such a large proportion of necessary secondary collisions. This view is, to some extent, substantiated by the very small absolute intensities of both ions at this pressure; long free paths for the electrons and ions going hand in hand.

The simplest primary process is then represented by $I_2 = I_2^+ + E^-$. The primary process involving the formation of I^+ may be either the spontaneous dissociation of the iodine molecule, simultaneous with its ionization, or it may be the ionization of the iodine atom formed by thermal dissociation at the filament. The former of these processes is, we believe, the principal one. While it is true that there would be a large percentage of atomic iodine present if the gas came to thermal equilibrium with the filament, it is, on the other hand, evident that on account of the clean-up of atomic iodine by the metallic walls[2] and the possibility of recombination on the different surfaces the amount of atomic iodine present in the ionization chamber could not be appreciably large. This is substantiated by a study of the disappearing potentials of the ions I^+ and I_2^+. Smyth and Compton and more recently Fruth[3] have found that the ionization potential for the atom is 8 volts while that for the molecule is 9.5 volts, a difference of 1.5 volts. In our work, there was no appreciable difference found between the disappearing potentials of I^+ and I_2^+. The I^+ cannot then be formed from the iodine atom in appreciable quantities. The only possibility left is the process $I_2 = I^+ + I + E^-$.

The formation of I_3^+ must be a secondary process. The second ratio in the above table clearly proves this. Here again there are two possible processes accounting for its formation, $I_2^+ + I_2 = I_3^+ + I$ and $I^+ + I_2 = I_3^+$. The former of these is undoubtedly the process occurring. The latter is ruled out by the necessity that the relative kinetic energy of the colliding I^+ ion and the I_2 molecule plus their internal energies be equal to one of the discrete quantum levels of the resulting I_3^+ ion.[4] Without energy dissipation through light emission or collision with a third body, such a process is impossible or at least extremely improbable. Only when the relative kinetic energies of the colliding particles are *exactly* equal to the energy of some quantum state of the resulting molecule can this process take place. While it is possible that infra-red light is given out we do not believe it to be the case, since no such spectrum due to recombination between atoms or molecules has, as yet, been observed. The process we are urging is principally a tertiary one

[2] Professor Franck has informed us of some unpublished work by Bonhoeffer on such a clean-up of atomic iodine.

[3] H. D. Smyth and K. T. Compton, Phys. Rev. **16**, 501 (1920); H. F. Fruth, Phys. Rev. **31**, 614 (1928).

[4] See Born and Franck, Zeits. f. Physik **31**, 410 (1925).

since most of the I_2^+ ions are themselves due to a secondary process. There should then be a larger rate of increase of the ratio I_3^+/I^+ with pressure. With a five or six-fold increase in pressure, there is about a ten-fold increase in the ratio I_3^+/I^+ while there is only a two-fold increase in the I_2^+/I^+ due to a secondary process for this same pressure change. The evidence favors the process $I_2^+ + I_2 = I_3^+ + I$.

The secondary formation of I_2^+ can only be $I^+ + I_2 = I_2^+ + I$, a collision in which the I^+ ion robs the I_2 molecule of an electron. That this process can take place it is necessary that either the I^+ ion is in an excited state or that the ionization potential for the formation of I^+ from atomic iodine is greater than that for the formation of I_2^+ from the molecule. It is rather improbable that sufficiently large numbers of the I^+ ion would remain in the excited state, so we must conclude that the iodine atom has a greater ionization potential than the iodine molecule has, to form unexcited I_2^+; a conclusion which, at first sight, appears contradictory to previous experimental work. Smyth and Compton, and Fruth[3] have shown that the formation of I^+ from atomic iodine requires 8 volts energy and that of I_2^+ from I_2, 9.5 volts. However, as Condon[5] has pointed out in the case of H_2, the I_2^+ formed by this process may very well retain a considerable amount of energy in vibrational form, an amount sufficient to make the ionization potential of I_2 to form *unexcited* I_2^+ actually smaller than that of the iodine atom. As we shall show later, the most probable transition is, we believe, one from the normal molecule I_2 to an I_2^+ ion with vibrational energy near the convergence limit of the vibrational states. That the normal level of I_2^+ is at least 1.5 volts below the convergence limit of the vibrational states, we can prove by thermodynamic argument. The process represented by Eq. (3) may be looked upon as the robbing of either an electron or an atom from the I_2 molecule by the I^+ ion. Both processes are thermodynamically equivalent. The heat of dissociation of the I_2^+ formed must be greater than 1.5 volts or this process of atom exchange could not occur. This value also represents the difference in the observed ionization potentials of Fruth. While the normal level of I_2^+ is not attainable by electron ionization, yet in a collision such as that above, this transition may be entirely possible; so that the ionization of the I_2 to the normal state of I_2^+ would then be lower than that of the iodine atom to form I^+.

It is difficult to draw conclusions regarding the formation of I^{++}. This ion was found only in small amounts. As the table shows, there is no systemic variation of I^{++}/I^+. It is probably the result of a primary process, with the I^{++} ions disappearing by secondary collisions, as does the I^+. The concentration of I^+ is so small in the ionization chamber as to preclude I^{++} formation by secondary electron ionization of this ion.

The disappearing potentials were obtained in the usual manner from plots of the intensities of the peaks against V_1. Corrections were made by using argon as the comparison gas, 15.4 volts being taken as its ionization

[5] Condon, Proc. Nat. Acad. **13**, 466 (1927).

potential. Seven determinations of the disappearing potentials of I_2^+ gave a mean of 9.3 volts with a maximum deviation of 0.3 volts. Taking into account the possible error introduced in the method of correcting for contact potentials, etc., the error may undoubtedly be somewhat larger than this. Three determinations of the disappearing potential of I^+ gave an identical value of 9.3 volts. While these absolute values may be somewhat in error, it is certain that they are identical within a few tenths of a volt. This we take as evidence that the most probable transition is from the normal molecule to an ionized one near the convergence limit of the vibrational states; those transitions beyond the convergence limit resulting in dissociation, and those below into the I_2^+ with vibrational energy almost equal to the convergence limit. This means that the I_2^+ ion has a larger moment of inertia than the normal I_2. We have already pointed out that the heat of dissociation of I_2^+ is greater than that of I_2. This combination is one which is seldom encountered in band spectra work.[6]

The disappearing potential of I^{++} obtained from a single determination was 35.0 volts. If we assume that it results from a primary process, then by subtracting the heat of dissociation (1.5 volts) and the ionizing potential of iodine atom (8 volts), we obtain 25.5 for the ionizing potential of I(II). This value is not as accurate as that for the other ions because of the smaller quantities present, and may be in error by a few volts.

Negative Ions

Three negative ions were found, I^-, I_2^-, and I_3^- with intensities of the same order of magnitude as those of the positive ions. The principal processes which result in the formation of these various ions we believe to be the following:

(5)	$I_2+E^-=I^-+I$	Primary
(6)	$I^-+I_2=I_2^-+I$	Secondary
(7)	$I_2^-+I_2=I_3^-+I$	Tertiary

The pressure-intensity data upon which we base our conclusions are given in Table II.

Table II. *Variation of the relative intensities of the ions* I^-, I_2^-, *and* I_3^-.

Pressure in mm Hg	1×10^{-4}	7×10^{-4}	4×10^{-3}
$\frac{\text{Intensity } I_2^-}{\text{Intensity } I^-}$	0.005	0.1	0.5
$\frac{\text{Intensity } I_3^-}{\text{Intensity } I_2^-}$	0.4	1.0	2.0
$\frac{\text{Intensity of } I^- \text{ from filament}}{\text{Intensity of } I^- \text{ from ionization chamber}}$	5.3	2.9	0.35

These results show conclusively that the formation of I^- is the only primary process. To demonstrate that the I^- was formed, both near or at the

[6] See Birge, Molecular Spectra, Int. Crit. Tables, in press.

filament and in the ionization chamber, V_1 was made large and two peaks were obtained, one for the I^- formed at the filament and one for those formed in the ionization chamber. With a constant magnetic field strength, the ratio e/m is proportional to V, the applied analyzing voltage, where V is the total field through which the ion falls. For those ions formed at the filament, V is the sum of V_1, V_2, and V_3; for those ions formed in the ionization chamber, it is equal to V_3 plus a portion of V_2, depending upon where in the chamber the ion is formed. The same total voltage must be applied to have ions of the same e/m value traverse the same path through the magnetic field. For those ions formed in the ionization chamber, V_3 must be larger than for those formed at the filament and two distinct peaks are thus obtained when V_1 is large, V_2 small and V_3 varied. By reversing the field V_2, that peak due to the ions formed in the ionization chamber, was obliterated, while that due to the ions formed at the filament was unaffected. The ions I_2^- and I_3^- were formed only in the ionization chamber.

Since I^- is formed by a primary process and as we have seen from the results on positive ions that there is no appreciable amount of atomic iodine present, the mechanism for the formation of I^- must be either $I_2+E^-=I^-+I$ or $I_2=I^-+I^+$. If the latter of these processes were the only one occurring, I^- would not be obtained at voltages lower than that necessary to produce I^+. The I^- ion has been obtained with electron voltages as low as 3 volts. These ions are undoubtedly also formed with electrons of zero velocity but it was always necessary to maintain a small voltage in the field to draw the negative ions along the path necessary for analysis, so fields less than 3 volts were impracticable. This alone does not eliminate the possibility that at higher voltages the latter process accompanies the former. We calculate that, if this were true, I^+ should be produced with electrons of 6 volts, assuming the electron affinity of atomic iodine to be 3.5 volts[7] and taking 8 volts as the ionization potential of the atom[8] and 1.5 volts[9] as the heat of dissociation of I_2. This is far outside the limit of error of our minimum value of 9.3 volts. Furthermore, we should expect that with the transition of an electron from one atom to the other in the iodine molecule, simultaneous dissociation would be improbable. In general, dissociation, simulataneous with any electron transition in a molecule occurrs only when the moment of inertia in the excited state is greater than that in the normal or initial state.[10] On account of the polar nature of the molecule resulting from the transtition of an electron from one atom to the other, we should expect the attraction between the positive and negative components of the molecule to be greater and hence the moment of inertia smaller; a condition under which simultaneous or spontaneous dissociation could not occur. Therefore, we believe, the first process, $I_2+E^-=I^-+I$ is the only primary one that occurs in the gaseous phase. If, as we believe

[7] Born, Verh. d. Deutch. Phys. Ges. **21**, 13 (1919); **21**, 679 (1919).

[8] Fruth, reference 3.

[9] Kuhn, Zeits. f. Physik **39**, 77 (1926).

[10] See Franck, Trans. Faraday Soc. **21**, 536 (1925).

this process occurs with electrons of zero velocity, then the electron affinity of atomic iodine must be greater than 1.5 volts, the heat of dissociation of the iodine molecule.

Since I_2^- is formed by secondary collision, the process can only be that represented by Eq. (6), $I^- + I_2 = I_2^- + I$. The rather surprising conclusion here is that the electron affinity of molecular iodine is greater than that of atomic iodine. It is important here to emphasize that the process $I_2 + E^- = I_2^-$ does *not* take place in spite of the tendency of this process to be greater energetically than that of the primary process (Eq. 5). As has been pointed out above, it would be necessary that radiation be emitted in this process. The evidence seems to be continually increasing that such double-collisional processes resulting in the formation of a single molecule never take place in chemical reactions. It might, however, seem reasonable to expect I_2^- ions to be formed in contact with the filament, contrary to experimental fact. We do not venture a guess as to the mechanism of the process occurring in contact with the filament. It is complicated on account of the filament's being at a relatively high temperature as well as being a source of electrons.

There are two possible processes for the formation of I_3^-: the one we have already given in Eq. (7), $I_2^- + I_2 = I_3^- + I$ and $I^- + I_2 = I_3^-$. Examination of the data given in the second line of Table II indicates that I_3^- is formed as a tertiary process, formed from I_2^- as represented in the former of the two possibilities given. The same triple-collision or light-emission argument used previously applies here against the latter process. It seems, perhaps, a bit surprising that the relative amount of I_3^- should be as great as it is, if it is formed by a tertiary process. However, this can easily be accounted for by assuming a mean free path of I_2^- slightly smaller than that of I^-, not an unreasonable assumption.

The possibility that any of the ions are formed on the surface of the gauzes is, we believe, ruled out by the reproducibility of the intensities of all of the ions.

Returning to the primary process (Eq. 5), it is interesting to speculate on the mechanism of the process occurring here. We have shown that this process occurs even when the electrons have considerable velocities, as high as 30 volts (no upper limit was determined). The very interesting question of the dissipation of the excess energy arises. If all of it is in the form of kinetic energy of the dissociating partners, it is difficult to picture such a mechanism in the way Franck[10] has done for the dissociation of molecules excited by light absorption or electron impact. If it is all emitted by radiation, why then is not I_2^- formed as a primary process? It may be a combination of these but none of these possibilities is reconcilable with any existing knowledge.[11]

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UNIVERSITY OF CALIFORNIA.
August 3, 1928.

[11] It has been suggested that the negative ions could be formed from the secondary electrons of the positive ion process. It is difficult to account for a sufficient number of such secondary electrons to give the large intensities of I ions observed here.

THE EFFECT OF WATER VAPOR ON THE MOBILITY OF GASEOUS IONS IN AIR

By Henry A. Erikson

Abstract

In this paper additional results are given which indicate that an H_2O molecule gives up an electron to the final positive air ion and thus forms an H_2O^+ ion of a greater mobility. Results are also given showing that the reciprocal of the mobility bears a linear relationship to the humidity.

IN AN earlier paper[1] attention was called to the effect of water vapor on the mobility of gaseous ions. It was there shown, as found earlier by Tyndall and Grindley,[2] that the mobility of the positive and negative ions in air diminishes as the amount of water vapor is increased. It was also there shown that when water was added to the air the number of initial positive ions (mobility 1.87) was increased at the expense of the number of final positive ions (mobility 1.36). In this paper results obtained under more favorable conditions are given which confirm the above. The arrangement of the apparatus was as shown in Fig. 1.

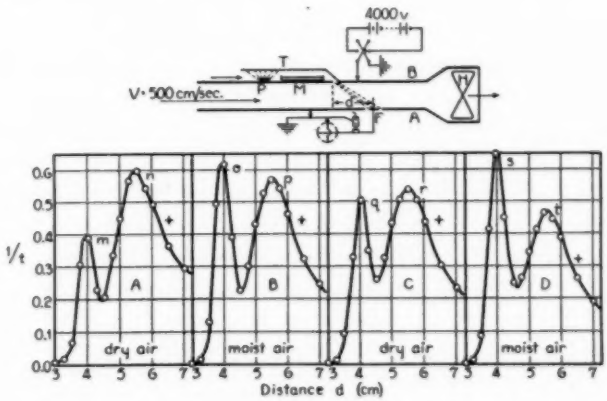

Fig. 1. Showing apparatus used and the increase in the number of initial positive ions when H_2O is added.

Air was drawn between the plates *A* and *B* which formed the bottom and top of a rectangular tube having ebonite sides. The distance between plates *A* and *B* was 3.5 cm. The width of this tube was 5 cm and its length 70 cm. The fan was driven by means of a cream-separator worm connected by a link belt to a synchronous motor. The speed of the air was of the order of 3000 cm/sec. The potential between plates *A* and *B* was of the order of 5000 volts and was obtained from a storage battery. The ions were pro-

[1] Erikson, Phys. Rev. **30**, 343 (1927).

[2] Tyndall and Grindley, Proc. Roy. Soc. **A110**, 358 (1926).

duced in the side tube T by means of a polonium plate at P, the position of which determines the age of the ions. M is a trough designed to hold water for humidifying the air.

Results Showing the Effect of Water on the Relative Number of Initial and Final Positive Ions

The polonium plate P was placed so as to give comparable numbers of the initial and final positive ions.

Curve A, Fig. 1, was obtained with no water in the trough M and normally dry air passing through the apparatus. The ordinates are proportional to the currents to the electrode F and the abscissae are the corresponding downstream distances of the electrode F. The maximum at m is for the initial positive ion (mobility 1.87 cm/sec per volt/cm) and maximum n is for the final positive ion (mobility 1.36 cm/sec per volt/cm).

Water was then placed in the trough M. The conditions otherwise remaining identical. The water, through evaporation, passed into the on-coming air stream containing the ions. Curve B, Fig. 1, was obtained under these conditions. The maximum o is for the initial positive 1.87 ion and the maximum p is for the final positive 1.36 ion. The rise in the maximum o shows that there was a marked increase in the number of initial ions, whereas the drop in the maximum p shows that the number of final positive ions decreased.

The positions of the polonium plate P and the trough M were then interchanged so that the trough was on the upstream side of P. In this case therefore the humid air was ionized. Curve C, Fig. 1, was obtained when there was no water in the trough. Maximum q is for the initial positive ions and r for the final positive ions. Water was then placed in the trough M and the curve D, Fig. 1, was obtained. The rise in the maximum s shows that again there was a marked increase in the number of initial positive ions and the lowering of the maximum t shows that there was a decrease in the number of final positive ions. No change was observed in the negative ion.

Interpretation

In earlier publications[3] the author has expressed his conviction that the initial positive 1.87 ion is one molecule large and that the final positive 1.36 ion is two molecules large. On this basis the above results mean that water increases the number of one-molecule ions at the expense of the two-molecule ions. The action no doubt is that a water molecule gives up an electron to the two-molecule air ion thus forming a one molecule H_2O positive ion. This process should be possible as the ionization potentials of nitrogen and oxygen are of the order of 16 volts, whereas the ionizing potential of H_2O is of the order of 13 volts. On the other hand recent results by Smyth and Stueckelberg[4] indicate the reverse process in the case of H_2O^+ and O_2. Since there are indications that O_2 has an ionization potential also of the order of

[3] Erikson, Phys. Rev. **28**, 372 (1926).

[4] Smyth and Stueckelberg, Phys. Rev. **32**, 779 (1928).

12 volts and since the final positive air ion is a double molecule complex of nitrogen or oxygen, it is not clear that the interpretation given above is in conflict with the results referred to.

That the initial air ion is similarly affected is of course fully as probable. This however can not be detected because only one-molecule bodies are involved thus giving rise to no change in mobility. Since all one-molecule ions have practically the same mobility in air, the ions H_2O^+, N_2^+ or O_2^+ can not be distinguished by mobility measurement.

Results Showing the Effect of Humidity in the Air on the Mobility of the Negative Air Ion

The essential part of the apparatus was the same as shown in Fig. 1. A large chamber was placed at each end of the tube as shown in Fig. 2. These were connected above so as to permit recirculating the air. Arrangement was made so that a dry bulb and a wet bulb thermometer could be inserted at Q in order to determine the amount of H_2O in the air.

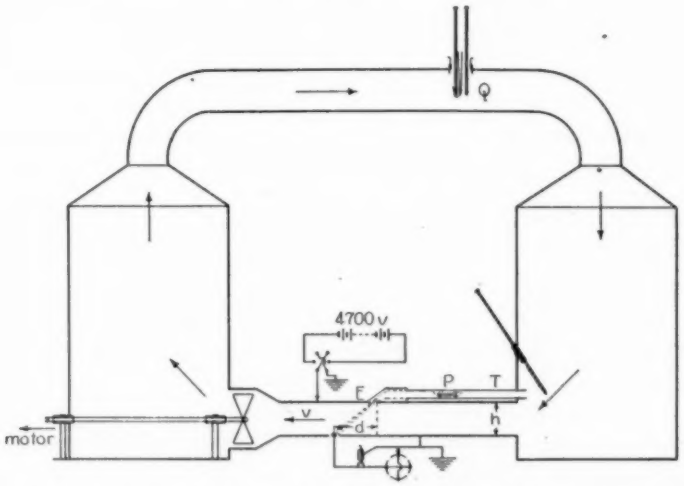

Fig. 2. Showing apparatus used in determining the effect of humidity on the ionic mobility.

As the mobility, in this case of constant air pressure, depends upon the temperature of the air it was necessary to keep the temperature from changing. This did not introduce a serious difficulty as the normal running equilibrium temperature was used which was about 5° higher than room temperature. The humidity was increased by approximately the desired amount by placing the required volume of distilled water in a copper boiler and evaporating it to dryness, allowing the vapor to pass into the apparatus.

The results are shown graphically in Fig. 3. The ordinates are the downstream distances (d) of the center of gravity of the curves obtained for each humidity. These are the average of the abscissae for all the points which are one centimeter apart on each curve.

The expression for the mobility is $k=h^2v/Vd$ or $d=h^2v/Vk$, where h is the distance between the plates, v the speed of the air, and V the potential between the plates.

Since d is proportional to the reciprocal of the mobility k, Fig. 3 shows that the relation between the humidity and this reciprocal of the mobility is linear. In terms of the quantities involved the expression for the mobility is $k=h^2v/V(lm+d_0)$ or $k=a/(lm+b)$, where d_0 is the distance at zero humidity,

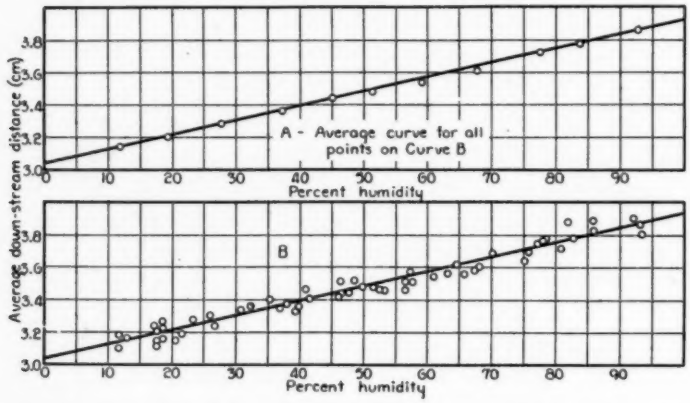

Fig. 3. Showing the linear relation between the percent humidity and the reciprocal of the mobility of the negative ion.

and m is the absolute humidity. This therefore agrees with Blanc's[5] law which may be expressed by the relation $k=a_1/(nc+b_1)$, where a_1 and b_1 are constants and c is the partial pressure.

Blanc's law is derived on the basis that the resistance to the motion of an ion is the sum of the resistances of the different gases present and that these partial resistances are proportional to the partial pressures and to the reciprocal of the mobility of the ion in these gases.

The linear relationship in this case apparently shows that the water vapor offers an independent resistance to the motion of the negative ion or in other words that the resistance to motion of water vapor is similar in character to the resistance introduced when CO_2 or H_2 is added to the air.

The author wishes to thank the Executive Committee of the Graduate School of the University of Minnesota for its financial aid in this research.

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UNIVERSITY OF MINNESOTA.
July 30, 1928.

[5] A. Blanc, Jour. d. Physique **7**, 825 (1908); S Loeb, Phys. Rev. **32**, 86 (1928).

EFFICIENCY OF IONIZATION IN HYDROGEN BY POSITIVE-ION IMPACT AT 7000 VOLTS

By Ronald W. Gurney

Abstract

Hydrogen at low pressure is bombarded with potassium positive ions of 7000 volts energy in a tube attached to a positive-ray box. Any hydrogen ions and scattered potassium ions passing into the latter are distinguished by mass analysis. The applicability of this method for measuring the efficiency of ionization is discussed. If the hydrogen molecules receive kinetic energy from the 7000-volt ions which ionize them, they will be scattered in all directions, and only those which happen to be projected towards the slit will enter the positive-ray box. But if ionization is unaccompanied by transfer of kinetic energy, the method is competent to compare the ionizing efficiency with that of electron-impact. With small positive-ion emissions no ionization was detected; with larger emissions a violent discharge took place through the tube. The conclusion reached is that either the ionizing efficiency is less than 1/150 of that of 50-volt electrons, or else that ionization is accompanied by transfer of kinetic energy.

IN EXPERIMENTS which have hitherto been made to study ionization of gases by positive-ion impact, the effect looked for seems always to have been masked by spurious effects. Although in bombarding a gas with electrons the presence of positively charged particles may be accepted as evidence of ionization, this method is of course excluded in the case of positive-ion impact, unless a method is provided for distinguishing the secondary ions from the primary. Horton and Davies,[1] and Hooper[2] who repeated the earlier work of Pawlow,[3] accordingly used the converse method, that of looking for the presence of electrons liberated from the gas by the positive ions. Unfortunately the liberation of electrons from the metal electrodes was found to mask completely the effect looked for, in helium up to 200 volts and in hydrogen up to 900 volts. Since vapor from stop-cock grease does not seem to have been excluded in either of these experiments it is possibile that this copious liberation of electrons came not from the metal but from an adsorbed layer.

If the gas bombarded is of different molecular weight from the ions of the primary beam, the presence of secondary ions can be shown by any method of mass analysis. In the experiments to be described a positive-ray box of the Dempster type was used together with the method of differential pumping employed by Smyth and others; a diagram will be found in a previous paper.[4] The source of positive ions was catalyst oxide, deposited on a platinum filament. An accelerating voltage applied between this filament and a nickel gauze directed a beam of ions down the axis of the tube, so that the

[1] Horton and Davies, Proc. Roy. Soc. **95**, 333 (1919).
[2] Hooper, J., Franklin Inst. **201**, 311 (1926).
[3] Pawlow, Proc. Roy. Soc. **90**, 348 (1914).
[4] Gurney, Phys. Rev. **32**, 467 (1928).

gas in the region above the slits was bombarded by the ions. The nickel parts were all outgassed by an induction furnace before assembling. The procedure for identifying any type of ion was that usually employed: the accelerating voltage between the two slits of the positive-ray box is varied over the range previously determined by calibration; on plotting the electrometer deflection against the applied voltage, the presence of a group of ions appears as a "peak." Before going into detail it will be well to consider the circumstance under which the method will be competent to measure the efficiency of ionization.

To pass through the second slit of the positive-ray box, an ion must have been travelling down nearly perpendicular to the upper slit. In the case of electron-impact this is easily achieved by drawing the ions down by a small collecting field; for the molecule ionized has a very small thermal velocity, and receives practically no kinetic energy from the electron which ionizes it. But from a positive ion possessing 7000 volts energy the molecule can receive a large amount of kinetic energy. If this occurs, the molecules will presumably be scattered over a hemisphere, and only those ions which happen to be projected nearly vertically downwards will be collected unless a huge collecting voltage be applied. But if a large collecting voltage were used, the ions formed at various distances from the slit would fall through very different amounts of potential, and would be spread out over a large range of velocity. On varying the field between the two slits of the positive-ray box no "peak" of secondary ions could be identified, especially if they have already received different amounts of energy from the positive ions which ionized them.

It is clear, therefore, that if the process of ionization resembles that by electron-impact in that no appreciable kinetic energy is transferred to the molecule ionized, then this method is competent to measure the ionizing efficiency. But in all other cases it is not competent.

Results

In the earlier experiments hydrogen at a pressure of 1.7×10^{-3} mm was maintained in the ionization chamber. It could be bombarded alternately with electrons of 50 volts or with potassium ions of 7000 volts energy. A fuse was inserted between the tube and the 7000-volt terminal of the constant-voltage kenetron set, which had been kindly loaned by the General Electric Company. The collecting voltage to draw the ions towards the slits was 50 volts.

First using electron bombardment with an emission of only 0.12 microampere, the H_2^+ peak was easily found and its height measured. Emission of positive ions was then started instead, and searches were made for hydrogen ions at various voltages of the primary beam up to 5000 volts, but without finding any peak outside the experimental error. A small emission of primary ions at 7000 volts was then used, and this emission was increased by steps. When the emission was raised to 0.65 microampere a discharge took place in the tube, and the fuse blew with a loud explosion. No hydrogen

ions had been detected at the lower emissions, and the ionizing efficiency must have been less than 1/60 of that of the 50-volt electrons used, as computed from the height of the smallest peak that would have been detected.

A lower pressure of hydrogen was then used, 8×10^{-4} mm. A positive ion emission of 1.1 microampere was maintained for some time at this pressure and 7000 volts. Search was made both for H_2^+ and H^+ ions, but none were found with certainty. When the readings of the electrometer were most consistent, it was found that the ionizing efficiency was certainly less than 1/150 of that of the 50-volt electrons. This value is again obtained by considering the height of the smallest peak that could be detected, and by assuming the width of the peak to be the same as that of the peak obtained by electron bombardment. But, as pointed out above, the peak may be many times wider. When larger emissions were tried at this voltage and pressure, a discharge always took place, and the fuse exploded.

This sudden discharge is presumably due to cumulative ionization. This may be caused by the liberation of electrons from the molecules of the gas by positive-ion impact, or may be due to electrons released from the electrodes either by the positive ions or by photoelectric action.

On the other hand, ionization may be taking place all the time but be undetected because of the transfer of momentum discussed above. In the apparatus described we were looking for ions drawn from the beam at a right angle, and there was the question whether it would be better to look for ions at some other angle. The source was therefore mounted so that the beam could be set at any angle, but the search for hydrogen ions was no more successful than before. This was to be expected, since if there were a considerable variation with angle this could only mean that the ions were being projected by the ionizing impact; and all the ions not actually projected through the second slit would be almost unaffected by the collecting field.

At the meeting of the American Physical Society, April 1927, a paper on ionization of HCl vapor by positive-ion impact was presented by W. M. Nielsen.[5] The method was the usual one of looking for negatively charged particles, which were said to have been found with impinging ions of only 34 volts energy. It was suggested that the HCl molecule was being dissociated into ionized components.

HCl vapor was accordingly substituted for the hydrogen, and a brief search was first made with the positive-ray box for H^+ ions and Cl^- ions, but without finding either. Then HCl^+ ions were looked for, but it was found that any such ions were being masked by the potassium ions from the primary beam, which were coming into the box in enormous quantities, after having been scattered around the walls of the nickel ionization chamber. When hydrogen was being studied this effect had been inappreciable because of the great difference in the atomic weight, and consequent difference in the value of the magnetic field required to bend the ions round the semicircle

[5] Nielsen, Phys. Rev. 29, 907 (1927).

to the Faraday cylinder. But the scattered potassium ions (and ions of sodium which was present in the source as an impurity) made it impossible to study gases of higher molecular weight. An investigation into this intense scattering of ions from metal surfaces was therefore made, an account of which has recently been published.[4] The study of gases has not been carried further.

Discussion

Compton and Van Voorhis[6] measured the ionizing efficiency of electrons in gases, and correlated their results with the kinetic theory mean free path of electrons. They found that in hydrogen (and other gases) the number of ionizing collisions for electrons from 50 to 300 volts was about one-quarter of the number of kinetic theory collisions. The number of ionizing collisions for positive-ion impact seems to be a much smaller fraction of the number of kinetic theory collisions. It is of course doubtful what is the minimum transfer of energy or momentum which counts as a "collision" in the kinetic theory. But a simple calculation shows how small a fraction of 7000 volts transferred would suffice to account for the negative results obtained in the present experiments.

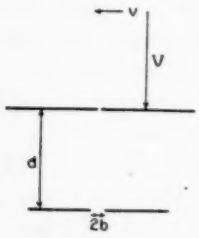

Fig. 1.

Let the half-width of the lower (wider) slit be b and the distance between the two slits be d. Let a molecule moving horizontally with a velocity v be ionized, and then acquire a velocity v' in falling through the collecting potential V. The condition for its getting through the second slit is approximately that v/v' be not greater than b/d. If E be the energy in volts corresponding to the velocity v, then $E/V = v^2/v'^2$ must not be greater than b^2/d^2. In the apparatus used $d = 10$ mm, $b = 0.2$ mm; so that $b^2/d^2 = 0.0004$. This means that the voltage applied must be 2,500 times the initial energy of the ion. This value may be halved to allow for the curvature of path produced by the other voltage applied between the two slits. This condition is just satisfied for thermal energies about 1/25 volt by applying 50 volts. But if the 7000 volt positive ions transfer as kinetic energy even less than one percent of their energy, i.e. less than 70 volts, it is clear that a very small yield could be obtained.

The conclusion reached then is that either the ionizing efficiency in hydrogen is less than 1/150 of that of 50-volt electrons, or that ionization is accompanied by transfer of kinetic energy.

This work was done during the tenure of a fellowship of the International Education Board, to whom my thanks are due. I also wish to express my thanks to Professor K. T. Compton and Professor H. D. Smyth for their interest in this work.

Palmer Physical Laboratory,
Princeton University,
July 23, 1928.

[6] Compton and Van Voorhis, Phys. Rev. **27**, 730 (1926).

SURFACE LAYERS ON TUNGSTEN AND THE ACTIVATION OF NITROGEN BY ELECTRON IMPACT[1]

By Carl Kenty and Louis A. Turner

Abstract

A fine tungsten filament at 400°C in active nitrogen is quickly covered with a layer which produces a lowering of the resistance of the filament. This lowering of the resistance is apparently the result of a lowering of the temperature of the filament which occurs because heat is more readily conducted away from the coated filament by the gas than from the clean filament. At a given temperature, 15–20 percent more heat is conducted away by the gas with the layer present. The same effect is produced by activating the nitrogen by bombardment with electrons. In a tube with a large nickel anode the production of the active agent could be detected down to 10.8 ± 0.5 volts. In a tube with a hot tungsten spiral anode of small area the effect could be detected down to the ionizing potential (16.3 volts). Traces of oxygen cause the spontaneous formation of a layer which renders the filament insensitive to active nitrogen. Traces of hydrogen prevent the formation of the nitrogen layer and remove it if already present. Experiments with a tube of small volume containing tungsten disks of large area show that the amount of nitrogen adsorbed is of the order of magnitude of the quantity necessary to produce a layer of single atoms. Activation of a stream of nitrogen reduces the thermionic emission from a tungsten filament in the stream. Similarly, the striking of an arc in nitrogen under suitable conditions gives a momentary slight increase of current followed by a great decrease, the emission apparently being cut down by the active form of nitrogen produced in the arc. Upon subsequent breaking of the same arc by reducing the anode voltage the current drops and then quickly rises to its much higher former value at that voltage. With an interrupted arc in pure nitrogen, and in argon containing a small percentage of nitrogen, an emission of the *D* lines persists for several hundredths of a second after the extinction of the arc. The sodium is evaporated from an oxide-coated filament and excited by some active form of nitrogen produced in the arc, presumably atomic nitrogen.

DURING an attempt to measure ionizing potentials in a stream of active nitrogen it was noticed that the thermionic current from a tungsten filament underwent a considerable temporary reduction as the activated nitrogen passed over it. Subsequent experiments, to be described below, have shown that this decrease was probably caused primarily by an increase of the work function of the filament, but it was thought at the time that the decrease of current might be accounted for as the result of the cooling of the filament by the active nitrogen, assuming the latter to contain nitrogen atoms and thus to have a thermal conductivity higher than that of ordinary nitrogen. Accordingly, a tungsten filament placed in the steam of nitrogen was connected as one arm of a Wheatstone bridge. The nitrogen could be activated by a condensed discharge passed between two tungsten electrodes up-stream from the filament. It was found that when the filament was white hot the active nitrogen increased the resistance slightly. When it was at a

[1] A preliminary account of these experiments was given in Nature, 120, 1927.

temperature of approximately 400°C, however, the active nitrogen caused a considerable lowering of its resistance which was permanent. This effect was permanent in the sense that the filament maintained its new lowered resistance after the activated nitrogen had passed on. This is, of course, contrary to what one would expect if the filament were to be cooled simply because of increased thermal conductivity of the active nitrogen, for this latter effect would last only as long as the active nitrogen were present. The permanent lowering of the resistance must have been the result of a change of the filament. It could be restored to its original condition by flashing it at a white heat.

For subsequent experiments the following simpler arrangement was used. The filament, which was of tungsten of a diameter of one mil and 2 cm long, was connected in series with a much larger resistance so that the current flowing through it was very little affected by small changes of its own resistance. The larger changes could be measured directly from the change in the voltage drop as measured by a voltmeter. Smaller changes were measured by a potentiometer, the voltage drop across the filament being balanced against a constant potential difference. A micro-ammeter was used as an indicating galvanometer. Any small change of the resistance of the filament would cause a proportional change in the voltage drop across it, thus putting the arrangement out of balance, the current through the micro-ammeter being to a first approximation proportional to the change of the resistance. The nitrogen used in these experiments was commercial nitrogen taken from a tank and passed over hot copper shavings. It still contained a small percentage of oxygen as was evidenced by the brilliance of the glow of active nitrogen. It was impossible to obtain a brilliant glow in the pure nitrogen used later.

The effect was investigated for various pressures ranging from 0.04 to 5 mm of Hg. It increased rapidly with pressure being negligible at 0.04 mm whereas at 5 mm the resistance of the filament changed by 20 percent. The relative changes of resistance were largest when the filament was at a temperature such that it was just perceptibly red in a dark room. If the filament were made much hotter the changes became temporary. The resistance would drop while the active nitrogen was present and then slowly recover its original value after the active nitrogen had passed.

The following experiment would seem to indicate that the effect of the active nitrogen is to form some kind of a layer upon the surface of the filament, rather than to change its volume conductivity. The resistance of the filament at room temperature was measured by ordinary methods. It was then warmed, treated with active nitrogen which caused the drop in its resistance and then allowed to cool to room temperature. Its resistance was then the same as it had been in the first place. That the effect of the active nitrogen had not been lost before this second measurement of the cold resistance was shown by warming the filament again, measuring the voltage drop across it, and then flashing it at white heat whereupon its resistance rose to the value it had had before the active nitrogen had passed over it.

The reduced resistance could not be, however, simply the result of the low specific resistance of a thin surface layer, for experiments described below indicate that this layer, if uniform, was of a thickness of the order of magnitude of atomic diameters and would thus have had to have an extremely low specific resistance at the higher temperatures in order to influence the measured resistance appreciably. At room temperature its specific resistance would have had to be much larger in order that the change in resistance caused by the presence of the layer should be inappreciable. Such hypothetical properties of the layer are fantastic. It seemed more reasonable to believe that in some way the layer caused a lowering of the temperature of the filament, the fall of resistance being only that which would be connected with such a change of temperature of any tungsten filament.

Such a cooling would result from an increase in the efficacy of any one of the processes by which heat is dissipated from a hot filament. Part of it is conducted away by the leads, part is radiated away, and part is conducted away by the gas. One would not expect the first process to be affected appreciably by the formation of a layer but the last two could be so affected.

The efficacy of the dissipation of the energy by radiation would have been increased if the layer had caused an increase of the emissive power of the surface. If this were the principal cause of the cooling however, one would have expected the effect to be most prominent for low pressures of gas for which the loss of heat by conduction by the gas would have been negligible in comparison with the loss by radiation. As mentioned above, the observed effect behaved in the opposite way, increasing rapidly with increasing pressure. The following experiment also gave a fairly direct indication that the presence of the layer did not increase the emissive power. A coarser tungsten wire was placed in the stream of nitrogen. Its surface could be cleaned by flashing it at a high temperature. A source of white light was arranged so that the light was reflected from this wire and could be observd with an eye-piece. The wire was flashed and then brought to a very dull red so that it was barely visible in the dark. After the activation of the nitrogen up-stream the wire became quite dark when the active nitrogen reached it showing that the layer was being formed and the wire cooled in the normal fashion. No change in intensity or color of the reflected white light could be detected, however, showing that the coefficient of absorption of the tungsten surface for visible light was not markedly affected by the presence of the layer. Since, according to Kirchhoff's law, the coefficient of absorption and the emissive power are in the same ratio to each other for all bodies at the same temperature it is evident that the formation of the layer did not produce any great increase of the emissive power of the filament for visible light. This was most probably also true for the infra-red radiation actually emitted by the warm filament, although not certainly so.

If it were possible to bring the filament to the same temperature for all pressures with and without the layer, one could study the conduction by the gas since the heat lost by conduction to the leads and by radiation would

be the same in all cases (assuming the emissive power to be the same with and without the layer). The changes in the energy supplied to the filament to maintain it at the given temperature would be the changes in the amounts of heat conducted away by the gas. This ideal experiment was realized to a first approximation by adjusting the current through the filament so that the resistance was always the same. Equal resistances would mean equal temperatures provided that the conductivity of the layer itself was negligibly small and that the variation of temperature along the filament was the same in all cases. The experiment described above indicates that the first condition was probably satisfied but undoubtedly with higher pressures and more energy being lost by the filament the variation of temperature along it was altered so that equal resistances gave equal temperature conditions of the filament to a first approximation only. Fig. 1 shows the results of the experiments. The abscissas are the pressures and the ordinates are the amounts of power supplied to the filament to bring it to a resistance of 14.2 ohms,

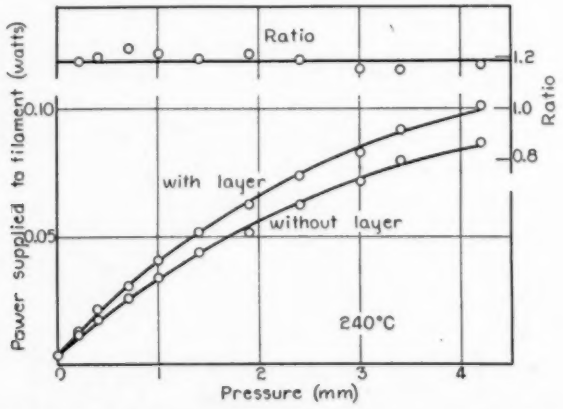

Fig. 1. Variation with pressure of the power input necessary to heat the filament to a resistance of 14.2 ohms (240°C).

corresponding to a temperature 240°C. The resistance of the leads was negligible. (The data for Fig. 1 were actually obtained by producing the layer by means of an arc in very pure nitrogen in the tube with the spiral anode described below. Results of the same sort but less complete were obtained with the ordinary active nitrogen. There was no reason to believe that there was any difference between the results obtained by forming the layer in the two different ways.)

The curve obtained with the layer present being higher, shows that heat was more readily conducted away by the gas when the layer was present. The fact that the intercepts of the two curves are the same indicates that the amount of energy radiated was not appreciably affected by the presence of the layer. Its small magnitude shows that the heat lost by conduction to the leads and by radiation was very small compared to that conducted away by the gas at the higher pressures. If it be assumed that this amount of power

was dissipated by metallic conduction and radiation at all pressures, the amounts dissipated by gas conduction are obtained by subtracting this intercept from the observed power values. These have been computed and the ratio of the two values obtained with and without the layer at each pressure also plotted in Fig. 1. Within the experimental error these values are all the same, the average being 1.19. The difference between the two curves must depend upon a difference in the effectiveness of the transfer of heat from the filament to the gas molecules since the thermal conductivity is a constant of the gas at a given pressure and is not dependent upon the properties of particular surfaces. The transfer of heat from solids to gases has been studied by many workers. Knudsen[2] introduced and defined the accommodation coefficient, the ratio of the amount of heat conducted away from the surface of a solid by a gas molecule to the amount which would have been conducted away had the gas molecule reached thermal equilibrium with the surface. Langmuir[3] showed that the value of the accommo-

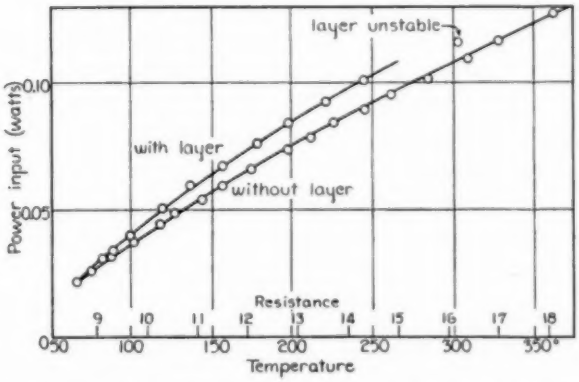

Fig. 2. Variation with temperature of the power input, with and without the layer, at 4.2 mm pressure.

dation coefficient for different surfaces and gases depended upon the presence of surface layers. The present experiments indicate that this coefficient is increased by the presence of the layer by about 19 percent at 240°. Our apparatus was not one such that it could be used to determine the actual value of the accommodation coefficient.

In order to see how this effect depended upon the temperature, readings of current and voltage were made from which could be calculated the power inputs for different resistances both with and without the layer at a pressure of 4.2 mm. The results are shown in Fig. 2. The temperatures were calculated roughly by the use of an average value of 0.005 for the linear coefficient of resistance of tungsten. The resistance at 22° was 7.15 ohms. The percentage increase caused by the layer seems to be very nearly constant for all temperatures down to 150° below which it seems to decrease.

[2] M. Knudsen, Ann. d. Physik **34,** 593 (1911).
[3] I. Langmuir, Phys. Rev. **8,** 149 (1916).

The experiments were not very accurate and show merely that there was no great change with changing temperature.

This cooling effect presents a sensitive indicator for the presence of extremely small concentrations of active nitrogen. It seemed that it would be of interest to endeavor to produce active nitrogen by electron bombardment and if possible to determine the critical voltage for its formation. A tube which had been designed originally for determing ionizing potentials by the Hertz-Kingdon method was used for these experiments. A diagram of the tube is shown in Fig. 3. F_1 is the source filament, a source of electrons which were accelerated by the voltage applied between it and the grid in the side of the cylindrical anode A. This was 4 cm in diameter and 8 cm long. F_2 was the filament which served as the detector of active nitrogen or as the source of a thermionic current limited by space charge when the tube was being used to measure the ionizing potential. The nickel anode was thoroughly de-gassed by the repeated use of an induction furnace. Experiments with this tube showed that there was a production of some layer-forming agent upon raising the voltage above approximately ten volts. Fig. 4 shows typical curves. The abscissas are the times and the ordinates are the readings of the micro-ammeter of the potentiometer circuit. Changes in the latter are proportional to changes in the resistance of the filament. Curve A shows how the resistance changed with time when no accelerating voltage was applied. The break in Curve B comes at the instant that the accelerating voltage from F_1 was applied.

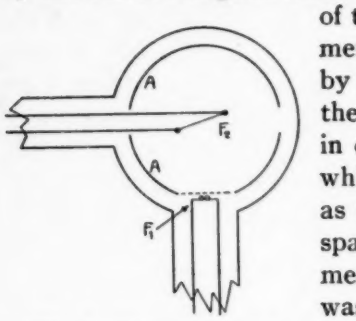

Fig. 3. Diagram of tube.

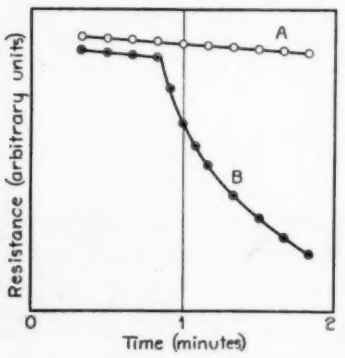

Fig. 4. Typical curves showing change of resistance of filament with time.

This fall in the resistance with no applied voltage was observed in many of these experiments and previous to the activation in all the experiments with ordinary active nitrogen. It indicates the formation of a layer by the unactivated gas. This can be attributed to the oxygen present as an impurity in the gas. It was found that if the gas was circulated through a tube containing a white-hot tungsten filament a deposit of blue tungsten oxide was formed and that the rate of formation of the layer on the test filament by the unexcited gas was steadily reduced. In all the later experiments pure nitrogen made by Waran's method was employed but even this contained enough oxygen to cause the spontaneous formation of a layer until it had been circulated for some time over the hot purifying filament. By the introduction of a very slight amount of oxygen (0.1 percent) the original condition could be restored and the whole series of effects repeated. When sufficient

oxygen was present the layer would form spontaneously so quickly that the resistance reached a steady value before the effect of activating the nitrogen could be tried. Under these conditions no further cooling was caused by the active nitrogen but occasionally a slight warming of the filament was detected. This may have been produced by the combination of nitrogen atoms at the surface or by some other chemical reaction. Experiments of this general sort were performed by Willey and Rideal[4] with filaments of various metals, including tungsten. They found that the active nitrogen heated all the metals but the effect was small for tungsten. Since they made no mention of flashing the filament immediately before each experiment in order to clean it, it may be that this was not done and that the effect which they observed was the same as ours with the already coated filament. Our experience indicates that this layer would probably have formed slowly in spite of the high purity of the nitrogen which they used. We also found that the addition of a slight amount of hydrogen would quickly clean off a nitro-

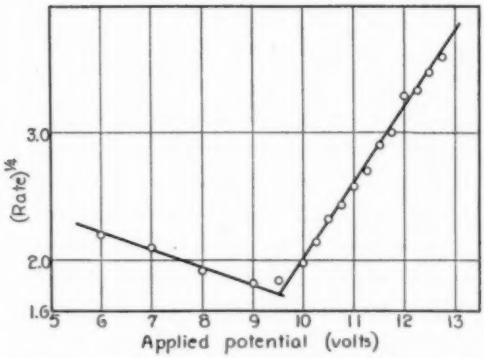

Fig. 5. Curve indicating critical potential for the formation of the active substance.

gen layer already formed and would prevent the formation of any further nitrogen layer. It did not seem to affect the oxygen layer. These experiments explained many puzzling, apparently contradictory results obtained before the effects of traces of oxygen and hydrogen were recognized as such. The experiments with oxygen suggest the use of such a test filament for the detection and measurement of small quantities of oxygen in other gases which do not affect the filament.

The nitrogen was activated by electron impact first with an oxide-coated platinum strip as a source of electrons and then with a tungsten filament for a source thus showing that the effect could not be attributed to anything being driven out of the oxide-coated filament by the bombardment of it by positive ions. The cooling effect obtained in this way showed the same increase with pressure as that obtained with ordinary active nitrogen. It persisted as the gas was made as pure as possible by circulating it through the tube containing the hot tungsten filament and through liquid air traps which kept mercury from the circulating pump from entering the tube. It

[4] E. J. B. Willey and E. K. Rideal, Jour. Chem. Soc. London, p. 2188 (1927).

was independent of the potential of the test filament, showing that the layer was formed by neutral atoms or molecules.

With the oxide-coated filament an attempt was made to determine the critical potential for the formation of the active substance. The time necessary for the micro-ammeter to change between two arbitrarily chosen values as the filament cooled was measured for each accelerating voltage, the filament having been flashed before each observation in order to remove any layer already accumulated. The reciprocals of these times gave measures of the rates of formation of the active substance. In Fig. 5 the fourth roots of these rates are plotted against the corresponding voltages. The fourth roots were chosen simply because two straight lines can be drawn through the points plotted in this way. The break indicates a critical potential of 9.5 volts but the determination of the ionizing potential in the same tube with the same gas at nearly the same time indicates that this value should be corrected to 10.8 ± 0.05 volts, assuming the value of the ionizing potential to be 16.3 volts.[5] The drop in the rate at the lower voltages is independent of the applied voltage, such a progressive change being shown by rates obtained with no applied voltage. It indicates a gradual purification of the gas during the course of the experiment.

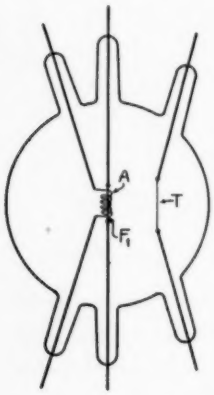

Fig. 6. Design of tube to reduce area of metal surface.

Because of the apparent extreme sensitivity of the test filament it seemed desirable to construct a tube in which there would be less metal surface in order to be free from any such effects which might arise from substances driven from the surface of the metal parts by bombardment by the accelerated electrons. The tube shown in Fig. 6 was constructed with this end in view. The straight filament F_1 was the source of the bombarding electrons. The anode A was coiled tungsten wire which could be kept hot so as to keep its surface clean. The test filament T was placed at the side as indicated. The tube was thoroughly baked out before any experiments were made. The results obtained with this tube were much the same as those obtained with the first one except that the ionizing potential was the minimum voltage at which any formation of the layer could be detected. The cooling effect was obtained when the anode was heated to a bright yellow temperature so as to drive off any layer which might have been formed upon it previously thus showing that the active substance was not produced by bombardment of the anode. It was also obtained when a strong magnetic field was produced along the axis of the filament F_1, preventing any electrons from striking the outer walls of the tube, thus eliminating the loosening of substances from the walls of the tube by electron bombardment as a possible explanation for the effect. It appears that the active layer-forming substance can be produced by bombardment of pure nitrogen by electrons having more than 16.3 volts of energy. The lower value obtained with the

[5] C. A. Mackay, Phil. Mag. **46**, 828 (1923).

tube containing the large nickel anode is presumably a critical value for the releasing of either oxygen or nitrogen from the surface of the nickel and it is nearly the same value as that found by Kistiakowsky[6] for the production of ions by the bombardment of various metals, including nickel, which had been exposed to nitrogen. He found that the adsorbed film formed upon the surface of a clean iron target very rapidly when a small amount of nitrogen was admitted to the tube, without activation. In the present experiment, however, the layer which forms spontaneously is apparently one of oxygen, upon the tungsten at least.

The use of a small test filament in a large volume is liable to give spurious results because with even a very small percentage of an impurity there is enough of it to coat a fine filament. It seemed desirable to construct an apparatus of small volume containing tungsten surfaces of large area so that the formation of a layer one atom deep on the tungsten surface would give a reduction of the pressure far in excess of the possible partial pressure of any impurity. An apparatus as indicated in Fig. 7 was made. The main bulb contained 42 circular tungsten disks supported on a heavy tungsten wire and kept apart by small rings made of tungsten wire. Each disk was 8 mm in diameter so that the total area of the tungsten surface was 42 sq cm. The nitrogen could be activated by passing a condensed spark between the two electrodes E or in a later experiment by running an arc between a hot filament and an anode put in above the disks. The filament F was put in in order to test for oxygen by cleaning it up with this filament. The pressure was measured by means of the previously calibrated hot-wire pressure gauge G of small volume. The total volume of the tube and gauge and connecting tubing to the trap which could be made to cut off the tube from connection with the pump was 18 cc. Assuming that a single nitrogen atom occupies an area of one square Angstrom unit (probably a little too small) it follows that there would be 4.2×10^{17} atoms in a uniform layer of single atoms covering the 42 sp cm of tungsten surface. If driven off these would give a pressure of

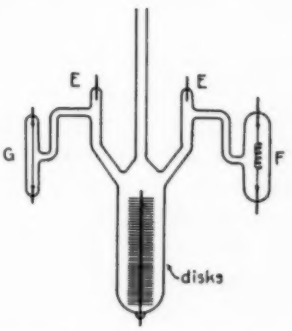

Fig. 7. Design of tube of small volume and large area of tungsten.

$$\frac{4\cdot2\cdot10^{17}\cdot760\cdot22.4\cdot10^{3}}{2\cdot6\cdot10^{23}\cdot18}=0.33 \text{ mm of } N_2$$

in this tube having a volume of 18 cc, such a pressure being easily measured with the gauge.

One complete experiment was made as follows. The tube was baked out at 440° for 3/4 of an hour. Nitrogen to a pressure of 1.9 mm was admitted to the tube and a spark passed between the electrodes, to drive gas out of

[6] G. B. Kistiakowsky, J. Phys. Chem. **30**, 1356 (1926).

them, until they were red hot. The bulb was kept at 330° during this process. The gas was pumped out and the process repeated. The filament F was freed of gas by heating it to a high temperature for some time and then the tungsten disks were out-gassed by heating them to a high temperature with the induction furnace. The system of small volume was then cut off from the pump and it was found that when the disks were glowed for a half minute at a high temperature that only a few hundredths of a mm of gas were given off. Pure nitrogen was then admitted to give a pressure of 1.9 mm and the system of small volume again shut off. While the disks were kept at a dull red by intermittent use of the induction furnace hot sparks were passed between the electrodes, also intermittently so as to avoid undue heating of the electrodes. After the tube had cooled it was found that the pressure had dropped to 1.4 mm. The tube was then evacuated and again shut off. The furnace was put around it and the tube heated to about 400° for 15 minutes and the filament flashed. Approximately 0.05 mm of gas were thus recovered. The tube was exhausted for 10 minutes being kept at a temperature of 400°. It was then immersed in liquid air, shut off again, and the disks heated yellow for about thirty seconds. This had to be done intermittently because of the necessity of replenishing the liquid air which boiled away rapidly. It was used in order to avoid the possible evolution of gas by the heating of the walls during the flashing of the disks. Approximately 0.2 mm of gas was thus recovered. The tube was immersed in water and the filament run at a bright yellow for 3/4 of an hour. There was no clean-up of the gas and no blackening of the walls of the tube as there would have been had the gas contained an appreciable quantity of oxygen or of water vapor. The spectrum of the gas was examined with a small hand spectroscope when it was excited by passing a spark between the electrodes. It gave the spectrum of nitrogen but the $H\alpha$ line was not present as it would have been had the gas contained a small amount of hydrogen or water vapor. It is thus seen that the amount of gas recovered was much greater than could be accounted for as an impurity in the supposedly pure nitrogen, it gave the spectrum of nitrogen, and did not behave as either oxygen or hydrogen would. The tungsten had adsorbed a quantity of nitrogen of the order of magnitude of the amount necessary to cover it with a single layer of atoms.

Further experiments of this sort showed that the layer was not put on the tungsten unless the nitrogen was activated by a hot spark or an arc and that the layer did not form as readily upon cold tungsten. Experiments with a similar bulb containing no tungsten showed that no gas could be recovered by heating the bulb after sparking although a small clean-up had been observed. Other similar experiments were made with a different tube containing a coiled heavy tungsten wire instead of the disks which could be heated by passing a current through it. The area of tungsten in this tube was only 18 sq cm so that the amounts of gas recovered were smaller but the ratios of the amounts recovered to the area of tungsten were nearly the same as before. The two tubes were of nearly the same size which shows that it was the area of the tungsten and not that of the glass which was important.

There is, of course, no proof that the cooling effects discussed above result from the formation of a layer like the one here studied but they were most readily understood as resulting from the formation of a layer such as the one whose existence is here demonstrated.

The original observation that the thermionic emission from a tungsten filament suffered a considerable temporary reduction as ordinary active nitrogen passed over it was repeated and the effect found when the nitrogen was more nearly free from oxygen than that originally used. A similar effect has been obtained with pure nitrogen activated by an arc discharge in the tube with the hot spiral anode described above (Fig. 6). As the voltage applied to the anode was raised the current increased in the normal way until a value in the neighborhood of the ionizing potential was reached. For voltages above that the current showed a tendency to fall off with time slowly, it being necessary to wait several minutes after raising the voltage before the current became steady. At about 26 volts an arc struck, the current showed an instantaneous increase and then quickly fell off to a

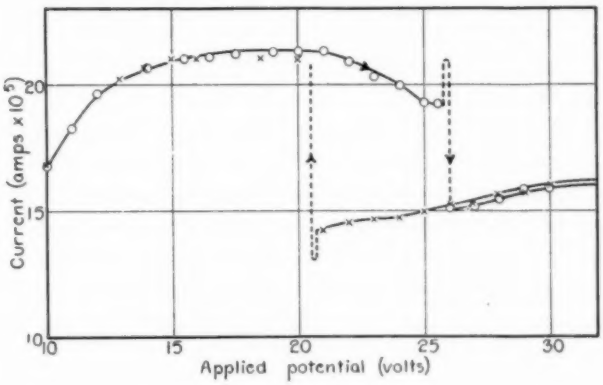

Fig. 8. Typical curve showing variation of thermionic current from a tungsten filament in pure nitrogen.

value lower than that which it had had before the arc struck. Further increases in the voltage produced increases in the current in a normal way. Upon decreasing the voltage the current fell off until the arc broke at a voltage lower than that at which it had struck. When the arc broke the current dropped instantaneously but then quickly rose to the value which it had had before at that voltage as the voltage was being raised. This current might be several times as large as it had been before the arc broke. For still lower voltages the same values of the current as at the beginning were obtained. Fig. 8 shows the actual currents in one particular typical experiment. If the pressure or the temperature of the filament was too high this effect was not observed. Several times it was possible to adjust conditions so that slow oscillations of a period of a second or so were obtained. The arc would strike, the current drop off until it would break again, the current then rise until it struck again, and so on.

The slow falling off of the current was accompanied by a slow cooling of the test filament present in the bulb, and the striking of the arc caused a very rapid cooling of the test filament, suggesting that both effects are evidences of the presence of the same active substance. The fall in the current would occur if a layer formed upon the surface of the hot filament increasing the work function for the surface. No cooling of the hot filament was observed so that the effect must be attributed to a change of the work function rather than to a diminution of the temperature. Langmuir[7] found such a diminution of the thermionic current but with much lower pressures of nitrogen and at higher voltages.

It has been suggested that this effect might be the result of the formation of charged layers on the surface of the bulb. We believe that this is not the case because such charged places would be effectively shielded by the formation of space-charge sheaths. Further, it has been found that there is no such effect with pure argon at the same pressure in the apparatus and with similar currents. If the argon contained a slight amount of nitrogen, however, indications of the beginning of such an effect were observed.

The filament which was the source of the electrons in these experiments was heated to a high temperature such as was reached in flashing the test filament of the earlier experiments in order to drive off the layer. The layer which was responsible for the drop of the thermionic emission must have been, therefore, a temporary one present only in an atmosphere of the active substance. This was shown by the rapidity with which the current rose to its former value after the breaking of the arc. (Fig. 8.) It has been shown that in certain other cases[8] the work function of a filament was greatly changed when but a small fraction of the surface was covered with atoms of a different sort. The same condition may hold here, the effect being produced by a layer covering but little of the surface.

Ordinary active nitrogen is probably a rather complicated mixture of various atoms and molecules,[9] so that from experiments with that alone it would be impossible even to guess what it was that produced the layer. The experiments with the gas activated by electron bombardment and those with the tube containing the disks show that the layer is one of nitrogen. The effective activated variety might be either atomic nitrogen or metastable excited nitrogen molecules. The experiments do not give any definite evidence conclusively in favor of either one of these possibilities but the fact that the large production of the layer-forming agent occurred in the neighborhood of 20 volts is suggestive since the experiments with positive rays[10] have indicated that atomic ions are produced at about 24 volts. These ions are produced by the breaking up of unstable molecular ions. It is not impossible that similar unstable excited molecules might be produced at lower

[7] I. Langmuir, Phys. Rev. **2**, 450 (1913).

[8] K. H. Kingdon, Phys. Rev. **24**, 510 (1924).

[9] J. Kaplan and G. Cario, Nature, **121**, 906 (1928).

[10] H. D. Smyth, Proc. Roy. Soc. **104A**, 121 (1923); T. R. Hogness and E. G. Lunn, Phys. Rev. **26**, 786 (1925).

voltages although there is no evidence for this. The cooling effect undoubtedly does begin close to the ionizing potential of nitrogen but may result from a further ionization of the relatively stable ordinary molecular ions.

Although the layer is produced by ordinary active nitrogen and by the electronically activated nitrogen it does not necessarily follow that the two varieties are the same. Experiments were made with heavy arcs in streaming nitrogen in an attempt to produce ordinary glowing active nitrogen in this way. They were unsuccessful but it is not surprising since ordinary active nitrogen could not be made to pass through a tube containing such hot metal electrodes. A tube was next arranged with a commutator so that it could be run intermittently, the space between the electrodes being examined spectroscopically, after the current was cut off, by use of a sectored disk on the shaft of the commutator. It was hoped that it might be possible to detect the after-glow bands characteristic of active nitrogen before it had disappeared. No indications of them were found when the space was viewed 0.0005 sec. after the arc had been cut off. The *D* lines were found to persist, however, several hundredths of a second if the voltage across the arc had been 21 volts or more but not for lower values. It was also noticed that the *D* lines could not be detected in the arc itself for voltages below 21. Some rearrangement of the arc took place and the current increased at that voltage. The sodium was apparently present in the oxide used in preparing the filament. These persistent *D* lines were found with mixtures of argon and nitrogen even when the amount of nitrogen was less than one percent but disappeared when the nitrogen was removed by circulating the gas through a tube containing a misch metal purifying arc. It was in the course of these experiments that the argon after-glow,[11] discussed elsewhere was noticed. Here again there is no direct proof of the presence of any particular variety of active nitrogen but the persistence of the *D* lines is greater than one would expect if they had been excited by collision with metastable molecules. It seems probable that the activated nitrogen formed by the impact of electrons is atomic nitrogen although this has not been conclusively established. It will be difficult to do so because so few of the properities of that elusive substance are definitely known.

In conclusion we wish to express our thanks to Professor K. T. Compton, Dr. K. K. Darrow, and Dr. Saul Dushman for helpful suggestions made by them in discussing this work with us.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
June 15, 1928.

[11] Carl Kenty, Phys. Rev. **32**, 624, (1928).

QUANTUM-MECHANICALLY CORRECT FORM OF HAMILTONIAN FUNCTION FOR CONSERVATIVE SYSTEMS

By Boris Podolsky*

Abstract

Dirac showed that, if in the Hamiltonian H momenta η_r conjugate to the coordinates ξ_r are replaced by $(h/2\pi i)\partial/\partial\xi_r$, the Schrödinger equation appropriate to the coordinate system ξ_r is $(H-E)\psi_\xi=0$. Applied to coordinate systems other than cartesian this usually leads to incorrect results. The difficulty is here traced partially to the way in which ψ_ξ is normalized and partly to the choice of H. In H expressions such as $qpq^{-1}p$ and p^2 are not equivalent, and the simplified form is generally incorrect. A formula satisfying all the requirements of quantum mechanics for a Hamiltonian of a conservative system, in an arbitrary coordinate system, is therefore developed

$$H=\frac{1}{2\mu}\sum_{r=1}^{r=n}\sum_{s=1}^{s=n} g^{-1/4}p_r g^{1/2}g^{rs}p_s g^{-1/4}+U$$

This formula is applied to a case of plane polar coordinates and leads to correct results.

SCHRÖDINGER,[1] and Eckart[2] have shown that the correct differential equation for the Schrödinger ψ function can be obtained if in the Hamiltonian function H we replace momenta p_x, p_y, and p_z by the differential operators $(h/2\pi i)\partial/\partial x$, $(h/2\pi i)\partial/\partial y$, and $(h/2\pi i)\partial/\partial z$ respectively and write

$$(H-E)\psi=0, \tag{1}$$

where E is the total energy of the system. Later the method was extended by Epstein[3] to non-conservative systems. Still later Dirac[4] has shown that, if ψ_ξ be regarded as the transformation function for transforming matrices from a scheme in which a set of coordinates ξ_r $(r=1, 2, \cdots n$, where n is the number of degrees of freedom) is represented by diagonal matrices to a scheme in which energy is a diagonal matrix, Eq. (1) will hold provided that in H we replace each momentum η_r, conjugate to ξ_r, by the differential operator $(h/2\pi i)\partial/\partial\xi_r$. Dirac's method of proof has an advantage in that it is valid even if ξ_r are not cartesian, but are any set of coordinates in which $\partial/\partial\xi_r$ has a meaning.

However, the application of this method to any but the cartesian coordinates leads almost invariably to erroneous results. To illustrate the difficulties, let us consider the case of the hydrogen atom in space polar coordinates.

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[1] E. Schrödinger, Ann. d. Physik **79**, 745 (1926).

[2] C. Eckart, Phys. Rev. **28**, 711 (1926).

[3] P. S. Epstein, Proc. Nat. Acad. Sci. **12**, 637 (1926).

[4] P. A. M. Dirac, Proc. Roy. Soc. **A113**, 621 (1927).

If we write the Schrödinger equation in cartesian coordinates

$$\nabla^2\psi_x(x,y,z) + \frac{8\pi^2\mu}{h^2}\left(E+\frac{e^2}{r}\right)\psi_x(x,y,z) = 0 \tag{2}$$

and transform this to polar coordinates, we obtain

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_x(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_x(r,\theta,\phi)}{\partial\theta}\right)$$
$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi_x(r,\theta,\phi)}{\partial\phi^2}+\frac{8\pi^2\mu}{h^2}\left(E+\frac{e^2}{r}\right)\psi_x(r,\theta,\phi)=0 \tag{3}$$

We have used the symbol ψ_x to indicate that, while in (2) ψ is regarded as a function of x, y, z, and in (3) as a function of r, θ, ϕ, it is the same function of position, so that

$$\psi_x(x,y,z)=\psi_x(r,\theta,\phi),$$

for the corresponding values of the coordinates. Eq. (3) is the equation used by Schrödinger in his treatment of the hydrogen atom.

If, however, we start with the Hamiltonian function in polar coordinates

$$H=\frac{1}{2\mu}\left\{p_r^2+\frac{1}{r^2}p_\theta^2+\frac{1}{r^2\sin^2\theta}p_\phi^2\right\}-\frac{e^2}{r} \tag{4}$$

and put $p_r=(h/2\pi i)\partial/\partial r$, $p_\theta=(h/2\pi i)\partial/\partial\theta$, $p_\phi=(h/2\pi i)\partial/\partial\phi$, Eq. (1) leads to

$$\frac{\partial^2\psi_r(r,\theta,\phi)}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2\psi_r(r,\theta,\phi)}{\partial\theta^2}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi_r(r,\theta,\phi)}{\partial\phi^2}$$
$$+\frac{8\pi^2\mu}{h^2}\left(E+\frac{e^2}{r}\right)\psi_r(r,\theta,\phi)=0, \tag{5}$$

which obviously differs from (3).

2. Part of the difficulty is due to the difference in the ways in which ψ_x and ψ_r are normalized. For ψ_x we have

$$\iiint\psi_x\psi_x^*dxdydz=\iiint\psi_x\psi_x^*r^2\sin\theta\,drd\theta d\phi=1 \tag{6}$$

while for ψ_r, according to Dirac,[5]

$$\iiint\psi_r\psi_r^*drd\theta d\phi=1 \tag{7}$$

integration being extended over the whole space. The relation between ψ_x and ψ_r must therefore be

$$\psi_x=(r^2\sin\theta)^{-1/2}\psi_r. \tag{8}$$

[5] P. A. M. Dirac, Proc. Roy. Soc. A113, 629 (1927).

If we substitute ψ_x from (8) into (3) we obtain a correct equation for ψ_r, which however is still inconsistent with (5).

We are thus led to the conclusion that (4) is not a quantum-mechanically correct Hamiltonian function. It is easy to see that one can put (4) into many classically equivalent forms which will differ greatly quantum-mechanically. Thus, a term such as p_r^2 may be written $r^{-1}p_r r p_r$, $r^{-1}p_r r^2 p_r r^{-1}$, $r p_r r^{-3} p_r r^2$, etc., which are not equivalent if p_r does not commute with r. We shall now develop a method of obtaining the quantum-mechanically correct form of the Hamiltonian function in an arbitrary coordinate system. In the present paper we shall restrict ourselves to non-relativistic conservative systems.

3. In a conservative system of N particles, if the kinetic energy of one, say kth, particle expressed as a function of coordinates $q_{1k}, q_{2k}, \cdots q_{nk}$ and momenta $p_{1k}, p_{2k}, \cdots p_{nk}$, is written for short $T_k(q_k, p_k)$, the Hamiltonian for the entire system may be written

$$H = \sum_{k=1}^{k=N} T_k(q_k, p_k) + U(q_{11}, q_{21}, \cdots, q_{n1}, q_{12}, \cdots, q_{nN}). \tag{9}$$

The potential energy U is not a function of momenta and will therefore be identical with its classical form. Thus, extension to systems with more than one particle involves merely a simple summation. Therefore, for the sake of simplicity, we limit ourselves to the case of a single moving particle, extension to the general case being obvious from (9).

4. The Schrödinger equation in cartesian coordinates of n dimensions, n being the number of degrees of freedom, is

$$\frac{\partial^2 \psi_x}{\partial x_1^2} + \frac{\partial^2 \psi_x}{\partial x_2^2} + \cdots + \frac{\partial^2 \psi_x}{\partial x_n^2} + \frac{8\pi^2 \mu}{h^2}(E - U_x)\psi_x = 0 \tag{10}$$

where ψ_x is supposed normalized so that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \psi_x \psi_x^* dx_1 dx_2 \cdots dx_n = 1 \tag{11}$$

An arbitrary coordinate system $u_1, u_2, \cdots u_n$ may be characterized by the coefficients, g_{rs} say, in the expression for the square of an element of length in terms of the u's, thus

$$\begin{aligned} ds^2 &= g_{11}du_1^2 + 2g_{12}du_1du_2 + \cdots + g_{22}du_2^2 + 2g_{23}du_2du_3 + \cdots + g_{nn}du_n^2 \\ &= \sum_{r=1}^{r=n} \sum_{s=1}^{s=n} g_{rs}du_r du_s, \quad g_{rs} = g_{sr}. \end{aligned} \tag{12}$$

As is usual, we will denote by g the determinant

$$g = \begin{vmatrix} g_{11} & g_{12} & g_{13} \cdots g_{1n} \\ g_{21} & g_{22} & g_{23} \cdots g_{2n} \\ \cdots & \cdots & \cdots \\ g_{n1} & g_{n2} & g_{n3} \cdots g_{nn} \end{vmatrix} \tag{13}$$

We shall also need the notation

$$g^{rs} = (\text{minor of } g_{rs} \text{ in } g)/g \tag{14}$$

We now wish to transform Eqs. (10) and (11) to the coordinate system u. In doing this, we regard $\psi_x\psi_x^*$, on account of its physical significance, as invariant function of position. Thus, in the expression for ψ_x we imagine $x_1, x_2, \cdots$ replaced by their values in terms of u's, so that

$$\psi_x(x_1, x_2, \cdots, x_n) = \psi_x(u_1, u_2, \cdots, u_n).$$

We retain the subscript x to distinguish this function of position from ψ_u which would be obtained by the use of (1) in the coordinate system u directly.

The formulae of transformation for expressions such as (10) and (11) are known.[6] We obtain

$$\sum_{r=1}^{r=n} \sum_{s=1}^{s=n} g^{-1/2} \frac{\partial}{\partial u_r}\left(g^{1/2} g^{rs} \frac{\partial \psi_x}{\partial u_s}\right) + \frac{8\pi^2\mu}{h^2}(E - U_u)\psi_x = 0 \tag{10'}$$

and

$$\int\int \cdots \int \psi_x \psi_x^* g^{1/2} du_1 du_2 \cdots du_n = 1. \tag{11'}$$

The corresponding normalizing equation for ψ_u is[5]

$$\int\int \cdots \int \psi_u \psi_u^* du_1 du_2 \cdots du_n = 1 \tag{15}$$

so that combining (11') and (15) we obtain

$$\int \int \cdots \int \psi_x \psi_x^* g^{1/2} du_1 du_2 \cdots du_n = \int \int \cdots \int \psi_u \psi_u^* du_1 du_2 \cdots du_n \tag{16}$$

Consideration of the way in which matrices are constructed, by the use of ψ_x and ψ_u respectively, shows that Eq.(16) must hold even if the integrands are both multiplied by an arbitrary function of u's. We must therefore have

$$\psi_x = g^{-1/4}\psi_u \tag{17}$$

Substituting ψ_x from (17) into (10') and multiplying the resulting equation by $-h^2 g^{1/4}/8\pi^2\mu$ we obtain

$$\frac{1}{2\mu} \sum_{r=1}^{r=n} \sum_{s=1}^{s=n} g^{-1/4} \frac{h}{2\pi i} \frac{\partial}{\partial u_r}\left(g^{1/2} g^{rs} \frac{h}{2\pi i} \frac{\partial}{\partial u_s} g^{-1/4}\psi_u\right) + U_u\psi_u - E\psi_u = 0 \tag{18}$$

This is in the form (1) and is therefore the desired differential equation for ψ_u. Replacing the differential operators $(h/2\pi i)\partial/\partial u$ by the corresponding

[6] F. D. Murnaghan, Vector Analysis and the Theory of Relativity, 46–48.

momenta, we obtain the expression for H in the quantum-mechanically correct form

$$H=\frac{1}{2\mu}\sum_{r=1}^{r=n}\sum_{s=1}^{s=n} g^{-1/4}p_r g^{1/2}g^{rs}p_s g^{-1/4}+U \tag{19}$$

In the classical case, when the order of factors is immaterial, this reduces to the usual form

$$H=\frac{1}{2\mu}\sum_{r=1}^{r=n}\sum_{s=1}^{s=n} g^{rs}p_r p_s+U \tag{20}$$

5. Let us apply these results to plane polar coordinates. Here $u_1=r$, $u_2=\theta$, $g_{11}=1$, $g_{22}=r^2$, $g_{12}=g_{21}=0$, $n=2$; therefore $g=r^2$, $g^{11}=1$, $g^{22}=1/r^2$, $g^{12}=g^{21}=0$. Using Eq. (19)

$$H=\frac{1}{2\mu}r^{-1/2}(p_1 r p_1 r^{-1/2}+p_2 r\cdot r^{-2}p_2 r^{-1/2})+U \tag{21}$$

This can be considerably simplified. Operating on ψ

$$\begin{aligned}
H\psi&=\frac{1}{2\mu}\left(\frac{h}{2\pi i}\right)^2 r^{-1/2}\left(\frac{\partial}{\partial r}r\frac{\partial}{\partial r}r^{-1/2}+\frac{\partial}{\partial\theta}r^{-1}\frac{\partial}{\partial\theta}r^{-1/2}\right)\psi+U\psi\\
&=\frac{1}{2\mu}\left(\frac{h}{2\pi i}\right)^2\left(\frac{\partial^2\psi}{\partial r^2}+\frac{1}{4}r^{-2}\psi+r^{-2}\frac{\partial^2\psi}{\partial\theta^2}\right)+U\psi\\
&=\frac{1}{2\mu}\left\{\left(\frac{h}{2\pi i}\frac{\partial}{\partial r}\right)^2+r^{-2}\left(\frac{h}{2\pi i}\frac{\partial}{\partial\theta}\right)^2-\frac{h^2}{16\pi^2}r^{-2}\right\}\psi+U\psi\\
&=\frac{1}{2\mu}\left\{p_r^2+r^{-2}\left(p_\theta^2-\frac{h^2}{16\pi^2}\right)\right\}\psi+U\psi
\end{aligned}$$

So that

$$H=\frac{1}{2\mu}\left\{p_r^2+r^{-2}\left(p_\theta^2-\frac{h^2}{16\pi^2}\right)\right\}+U, \tag{22}$$

which is just the Hamiltonian used by Dirac[7] in agreement with Pauli,[8] but it is here obtained without any special assumptions.

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BERKELEY, CALIFORNIA,
July 20, 1928.

[7] P. A. M. Dirac, Proc. Roy. Soc. **A110**, 561 (1926).
[8] W. Pauli, Zeits. f. Physik **36**, 336 (1926).

THE ABSENCE OF EFFECT OF AN ELECTRIC FIELD ON THE MAGNETIC SUSCEPTIBILITIES OF HCl AND NO

By L. M. Mott-Smith

Abstract

An experiment has been performed to test whether the magnetic susceptibilities of the polar gases, nitric oxide and hydrogen chloride, change on application of an electric field of about 8000 volts per cm. The susceptibility was investigated both parallel and perpendicular to the electric field, and its value was found to remain unchanged in every case. The following percent change in the volume susceptibility would have been detected: for NO, along the field, 0.18%, perpendicular to it, 0.48%; for HCl, parallel to the field, 9.7%, and perpendicular to it, 22%. When measuring the susceptibility of NO along the electric field a change in its value can only be expected to be due to the magneto-electric directive effect. An elementary classical theory indicates that in this experiment a 13% change in susceptibility is expected. The experiment is a repetition in the inverse manner of that of Huber on this effect, and confirms his negative result. The measurement of the susceptibility of NO perpendicular to the electric field is a confirmation for the case of the susceptibility of the theoretical prediction that the paramagnetic susceptibility and the dielectric constant of a polar molecule should be independent of an additional applied field which changes the axis of spatial quantization. With the diamagnetic HCl, it was supposed that a slight change in the susceptibility might be produced by the electric forces, but no theory has been attempted.

I. Introduction

IN THIS paper will be reported an experimental study of the effect of a strong electric field on the magnetic susceptibility of the two typical polar gases hydrogen chloride and nitric oxide. A change in susceptibility has been looked for both along the electric field and perpendicular to it.

In the experiments with the paramagnetic gas, NO, and when looking for a change in magnetic polarization along the electric field, an expected change can only be due to the magneto-electric directive effect. The alignment by a magnetic field of molecules having both an electric and a magnetic moment not mutually perpendicular should produce an electric polarization along the field. Evidently the inverse effect should also take place. The experiments looking for an electric polarization have been carried out by Huber[1] and the theory discussed by Debye and Huber.[2] It was thought interesting to repeat this experiment since Huber's unexpected negative result leads to the interesting consequence suggested by de Haas that there must exist two kinds of molecules having mutually opposite directions of magnetic moment relative to the electric dipole axis. An elementary classical theory for this case will be given, which indicates that in this experiment a large effect is expected.

[1] A. Huber, Phys. Zeits. **27**, 619 (1926).

[2] Debye and Huber, Physica **5**, 377 (1925); see also abstract, Phys. Berichte, **7**, 1044 (1926), A. Huber, Phys. Zeits. **27**, 619 (1926).

When the susceptibility is measured perpendicular to the electric field the experiment with NO is a test of the theoretical result obtained by Van Vleck, Kronig, and Pauling[3] by the matrix theory that the paramagnetic susceptibility and the dielectric constant of polar molecules should not depend on an applied field which changes the direction of spatial quantization. These writers consider only the effect of a magnetic field on the dielectric constant but the inverse must also be true since the same theory applies in both cases. This result has already been experimentally confirmed for the dielectric constants by the experiments of Weatherby and Wolf[4] and those of C. R. Daily and the author,[5] where a change in dielectric constant on application of a magnetic field was looked for.

The experiments with the diamagnetic HCl were considered interesting because it was considered that in the case of a molecule a slight change in the induced diamagnetic polarization might be produced by the electric forces.

II. Experimental Method and Apparatus

1. *Method.* The change in susceptibility produced by the application of the electric field is measured. This change is determined by measuring the change in force on a chamber containing the gas placed in a non-homogeneous

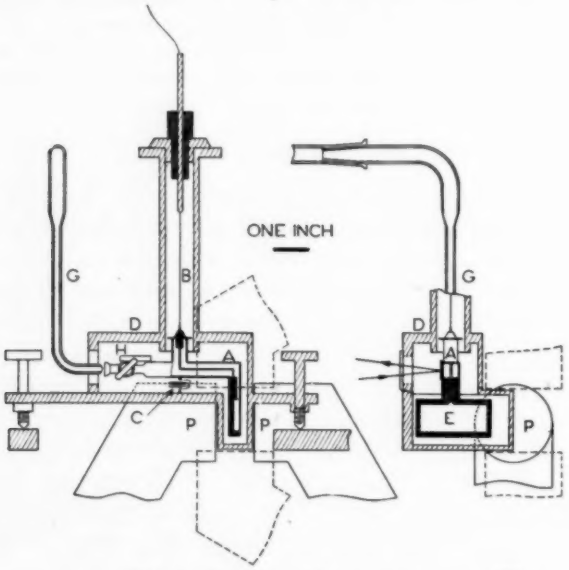


Fig. 1. Diagram of apparatus.

magnetic field. For measuring the force, the chamber is attached to the arm of a torsion balance arrangement which enables the measurement of the horizontal force by determining the angular displacement. The electric field is applied between one side of the metal chamber and an interior elec-

[3] J. H. Van Vleck, Nature **118**, 226 (1926); Phys. Rev. **29**, 727 (1927); *ibid.* **30**, 31 (1927) R. de. L. Kronig, Proc. Nat. Acad. **12**, 488 (1926); L. Pauling, Phys. Rev. **28**, 976 (1926).

[4] B. B. Weatherby and A. Wolf, Phys. Rev. **27**, 769 (1926).

[5] L. M. Mott-Smith and C. R. Daily, Phys. Rev. **28**, 976 (1926).

trode, the source of potential making contact with this electrode by way of the torsion fiber.

2. *Apparatus.* The details of construction are shown in Fig. 1. The chamber and torsion arm *A* are constructed of 0.002 inch (0.0051 cm) thick pure gold foil in the shape and of dimensions shown. The joints are crimped together and sealed with paraffin wax, which was found sufficiently resistant to the chemical action of the gases. The various parts of the box were fastened together with soft solder at a few spots for good electrical contact. The apparatus is suspended from the phosphor bronze strip *B* and is grounded by the lower spiral suspension *C*. The entire apparatus is enclosed in a heavy brass box *D* which carries the torsion head and is provided with levelling screws. The interior charged electrode *E* is supported on a paraffin block and is connected to the torsion fiber by a lead which passes down the tubular torsion arm and out through a quartz bushing. It is seen that the electrode and lead are completely enclosed by the grounded chamber and consequently no electrostatic forces are expected. The electrostatic effect was further much reduced by a disk which screens the field of the fiber from the unsymmetrical torsion arm. The final adjustment for no electrostatic effect was made by slightly changing the position of the apparatus relative to the outer box by adjusting the levelling screws.

The angular displacement of the torsion arm was read with a telescope and scale. The distance from mirror to scale was one meter and the deflections could be read to 0.1 mm.

The gases were generated, purified, and dried by standard methods. Care was taken to have nothing in the generating apparatus and gas-chamber with which the gases could react because it was found that contamination of the gas usually resulted in a very undesirable electrical leakage of the insulation. Since NO reacts with rubber and ordinary waxes the entire apparatus was put together without rubber tubing and using only paraffin wax where waxing was necessary. It was found that a satisfactory inert stopcock grease can be made by mixing soft paraffin with heavy pure paraffin oil (Nujol).

The gases are introduced into the chamber by means of a swinging glass arm *G* which connects with the stopcock *H* on the far end of the torsion arm by means of a small ground ball joint. A small hole in a lower corner of the gas-chamber allows it to be flushed out with the gas. This hole is closed by simply covering with paraffin.

The magnetic field was produced by an electromagnet having flat pole faces 5.7 cm in diameter placed so that one end of the gas-chamber was in the region of strong field between the poles and the other in the weaker field outside. In the experiments with the magnetic field parallel to the electric the poles are situated approximately as shown in solid lines in Fig. 1; for the parallel case the magnet was rotated through 90° about a horizontal axis to the position shown in dotted lines. This magnetic field of course produced a large force on the chamber due to the chamber's own susceptibility and that of the contained gas. It was necessary to eliminate this force as far as

possible and this was done by adding to the gas-chamber bits of material of suitable susceptibility. For this purpose a convenient substance was found to be a mixture of a small quantity of nickel dust with soft wax, since the chamber itself was strongly diamagnetic on account of the comparatively large amount of paraffin wax present.

III. Experimental Procedure and Results

1. *Procedure.* The procedure for making a measurement will now be clear. The gas is allowed to pass through the chamber for a few minutes, then the stopcock is closed, the hole sealed up, and the supply tube swung away.

It is next necessary to adjust the susceptibility of the chamber to nearly zero, and this is done by adding or removing bits of the special wax. However, since the susceptibility of the nickel filings depends on the field strength a convenient way to make the final adjustment is slightly to alter the strength of the magnetic field. In this way the zero of the torsion balance is brought near to its zero in absence of the magnetic field.

In order to guard against a possible additional restoring torque due to the magnetic forces, an effect which might seriously reduce the sensitivity, a method for testing the amount of this restoring torque was used. This method consisted in rotating the upper end of the suspension through a known small angle while the magnetic field is on and noting the angular displacement of the torsion arm. By comparing the deflection obtained with that found in absence of field, the amount of restoring torque due to the magnetic field can be determined. It was found that this restoring torque sometimes increased and sometimes reduced the sensitivity, but in all the measurements it was made nearly zero by proper disposition of the balancing wax.

The deflection due to the electrostatic field alone must next be reduced as much as possible. The disturbance caused by the introduction of the gas usually necessitated a readjustment of the level of the case. The electrostatic deflections were usually reduced to less than 0.1 mm. They were carefully determined by averaging with field on and with it off, several end-points of the small amplitude vibrations which the balance was usually describing. As a check, this determination was repeated after a measurement had been made with the magnetic field on.

The measurement of the effect consisted in taking readings of the position of the torsion arm at half minute intervals and switching the electric field on and off at two or three minute intervals. This procedure was necessary in order to be able to average out a steady creep which was always present. This motion was caused, no doubt, partly by the warming up of the electromagnet and partly by the decrease in the e.m.f. of the storage batteries supplying the current. The field was alternately put on in one direction and then reversed in order to eliminate a possible spurious effect which will be explained below.

2. *Spurious effects.* The most serious possibility for a spurious effect is a deflection produced by the magnetic force on the leakage current through

the gas and across the insulation. This effect is expected to be larger when the magnetic fields are perpendicular than when they are parallel because the probable direction of the force is such as to be more effective in producing a torque on the suspended system. For the perpendicular case this torque can be calculated, assuming the leakage current to be in the direction of the electric field between the electrode and the chamber wall, and using the average value of the magnetic field (1400 gauss). It is found that a current of 3.9 microamperes will produce the smallest readable deflection of 0.1 mm. During all the measurements the leakage current was read on a microammeter and was always less than 0.2 microamperes, and hence this effect is negligible. Furthermore it is possible in the perpendicular case to average out this effect by making measurements with the electric field reversed, because the leakage current force reverses but it is evident from symmetry that the effect of the field on the susceptibility must remain unchanged. In the parallel case this is not possible because the real effect also reverses, but here, since only a small component of the force can be effective in producing a rotation of the torsion arm, this effect must be entirely negligible.

Another effect which might cause a spurious deflection is a reduction in the size of the gas-chamber due to the electrostatic attraction between the electrode and the side. By actual measurement with a microscope it was found that the change in size was not serious.

3. *Sensitivity calculation.* The calculation of the deflection to be expected from a change in the susceptibility of the gas is easily made from the dimensions of the apparatus, the torsion constant of the fiber, and the strength of the magnetic field at the inner and outer ends of the chamber. The average value of the field at the two points was obtained by means of a fluxmeter and snatch coil and is given in the fourth and fifth columns of the table. The restoring torque of the fiber was found by attaching to it a body of known moment of inertia and obtaining the time of vibration. It was found to be

TABLE I. *Susceptibilities measured perpendicular and parallel to the electric field.*

Gas	No. of trials	Averaged deflection (cm)	Probable error (cm)	Magnetic field strength (gauss) H_1	H_2	Electric field strength V/cm	Vol. susceptibility $\chi \times 10^6$	Detectible % change
			Susceptibility perpendicular to electric field					
Air	32	0.001	0.001	2240	620	8600	+.030	0.85
H_2	4	.013	.003	2200	610	8600	−.0002	130.
NO	16	.007	.002	2100	580	8300	+.061	0.48
HCl	8	.002	.002	2300	630	7400	−.0011*	22.
			Susceptibility along electric field					
Air	6	.001	.002	3400	1150	8000	+.030	0.39
NO	8	.004	.006	3560	1270	8000	+.061	0.18
HCl	4	.001	.005	3450	1200	8300	−.0011	9.7

* Due to lack of experimental data, this value had to be estimated by interpolating between the values of the diamagnetic susceptibility of argon and Cl^-, between which it should lie. See "The Theoretical Prediction of the Physical Properties of Many Electron Atoms and, Ions. Mole Refraction, Diamagnetic Susceptibility, and Extension in Space," L. Pauling Proc. Roy. Soc., A, **181**, 114 (1927).

19.6 C.G.S. units. The formula $\Delta F = \frac{1}{2}a\Delta\chi(H_1^2 - H_2^2)$ was used, where ΔF is the change in force produced by a change in susceptibility $\Delta\chi$, where a is the area of section of the gas-chamber and H_1, H_2, are the average values of the magnetic field at the inner and outer ends of the chamber.

4. *Results.* Since the apparatus cannot be evacuated and there is some solid dielectric present which might cause an effect it was necessary to make determinations with gases in which no effect is expected. Air and hydrogen were used for this purpose.

All the results are shown in Table I. In the third column is shown the average deflection after correcting for deflection due to the electric field alone and including all the determinations. It is seen that these deflections come out very small in every case. The next column shows the probable error computed by dividing the average deviation by the square root of the number of observations. Although this quantity cannot represent the true probable error on account of the small number of observations, it gives an idea of the magnitude of the deviations of the observed deflections from the mean value. It is seen that the error is in most cases larger than the average deflection. But since there probably are systematic errors which will give deflections as large as these, the results can in no case be interpreted as indicating a real effect. However, it is possible to say that these experiments show definitely that there is no effect which can produce a deflection of 0.02 cm. The percent change in susceptibility corresponding to this deflection is shown in the ninth column, the value of the susceptibility used appearing in the preceding column.

IV. Theory for Magneto-electric Directive Effect

A simple calculation of the magnitude of the effect to be expected in this case can be made by slightly modifying Langevin's simple theory of paramagnetism. Assume a molecule having parallel electric and magnetic dipoles of strength μ_e and μ_m respectively. It is not necessary to assume that μ_e and μ_m make an angle with each other, because it is easily seen that the result depends only on the component of μ_e along μ_m, so that the only effect of an angle between the moments is to reduce this component. Let N such molecules occupy unit volume and let there be present a magnetic field of strength H and a parallel electric field of strength E. On account of the additional couple due to the electric force the potential energy of a molecule which makes an angle θ with the direction of the fields will now be given by

$$V = -(\mu_m H \pm \mu_e E)\cos\theta$$

The $\pm$ sign is introduced for also taking into account the case when the electric and magnetic moments are oppositely directed. Since the form of V remains unchanged, the usual development for calculating the average magnetic polarization can be used. Only the first order terms are needed, and we obtain for the polarization per unit volume,

$$P = \mu_m N(\mu_m H \pm \mu_e E)/3kT$$

Since the experimental results have been given in terms of susceptibility (χ), we introduce $\chi = P/H$ and find

$$\chi = \mu_m^2 N(1 \pm \mu_e E/\mu_m H)/3kT$$

It is evident that the term $\pm\mu_e E/\mu_m H$ is responsible for the change in susceptibility expected on application of the electric field. For NO, using the value, $\mu_e = 2\times10^{-19}$ and $\mu_m = 1.7\times10^{-20}$ used by Huber, and the values of the fields used in this experiment, it is found that $\mu_e E/\mu_m H = 0.13$. Thus the susceptibility should be increased or reduced 13 percent by applying the electric field. It is seen from the table that no effect was found, though a change of 0.18 percent could have been detected. However, if half the molecules have relative values of their moments corresponding to the + sign and half to the − sign it is seen that no effect can be expected. Now the analysis[6] by means of quantum mechanics of the so-called phenomenon of "sigma-type doubling" in molecular spectra shows that the component of electronic angular momentum and hence magnetic moment parallel to the axis of figure continually oscillates in sign. This is due to a quantum resonance between the left and right-handed states, so that a given molecule is in a certain sense alternately left and right-handed, making the + and − values of the magnetic moment equally probable. Thus there should be on the average no correlation between the directions of electric and magnetic moment, in agreement with the negative result found in this experiment and in Huber's. Before the mathematical study of sigma-type doubling, the best theoretical explanation of the null effect was probably to assume equal numbers of two kinds of molecules, respectively left and right-handed,[7] but the more recent theory[6] seems to show that even an individual molecule has on the average no discrimination between the left and right-handed rotations.

V. Conclusion

The experiment on the magneto-electric directive effect yields the result that no magnetic polarization of NO along an electric field of the magnitude expected by a Langevin theory is found. This result is in agreement with Huber's experiment and strengthens the assumption that there is no preference between left- and right-handed molecules.

The result that no change in susceptibility of NO perpendicular to the applied electric field was found agrees entirely with the quantum mechanics of these effects.

This result can be considered as favoring the new quantum theory, for it seems probable that the old quantum theory would have predicted a change in susceptibility just as was found by Pauling[8] for the dielectric constant in the inverse experiment.

I wish to acknowledge my indebtedness to Professors H. A. Wilson and Linus Pauling for many valuable suggestions.

The Rice Institute,
Houston, Texas,
July 1, 1928.

[6] R. de L. Kronig, Zeits. f. Physik **46**, 814 (1928); E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 267 (1928); also forthcoming papers by Kronig and by Van Vleck.

[7] Cf., for instance, J. H. Van Vleck, Phys. Rev. **30**, 40 (1927), and references.

[8] Linus Pauling, Phys. Rev. **27**, 568 (1926).

HALL EFFECT AND MAGNETIC INDUCTION IN A BAR OF ELECTROLYTIC IRON

By Emerson M. Pugh

Abstract

The Hall effect was measured in a bar of electrolytic iron in contrast to the usual method of measuring it in thin sheets of the material. Direct measurements were taken at the same time of the magnetic induction B and of the Hall e.m.f. E.

The E-*vs.*-B curve is a straight line up to $B = 12{,}000$ gauss where its slope starts to decrease. The curve of permeability-*vs.*-B has its maximum at this same value of B. Measurements taken at points on a "hysteresis loop" indicate that E is also proportional to B when the magnetizing force has been removed and only the residual B remains. The Hall coefficient for this bar is found to be only 20 percent lower than that found by A. W. Smith for electrolytic iron, if in its calculation the value of B is substituted for H in the usual formula.

Introduction

MEASUREMENTS of the Hall effect in different materials have shown that if the current in the material is kept constant, the Hall e.m.f. varies linearly with the magnetic induction in non-magnetic substances. In magnetic substances, however, the ratio of the Hall e.m.f. to the magnetic induction is constant only for values of the induction below a certain point, which is sometimes called the "saturation point." Above this point the ratio decreases.

This breaking of the curve away from a straight line was thought to occur when the substance was magnetically saturated, but this had not been verified since no experiments had been performed in which the B-*vs*-H curve and the Hall effect were investigated in the same piece of material. The reason that this had not been done is obvious when we consider that the best shape of material for measuring the Hall e.m.f. is a very thin sheet in which it would be quite difficult to investigate the magnetization curve.

The fact that many experimenters[1] have found large variations in the Hall coefficient for extremely thin sheets, and that W. van B. Roberts[2] found a Hall coefficient in his cylinder of bismuth which was only 1/3 of the value generally found for bismuth suggested there might be a much different value for the coefficient in a bar from that usually found for iron in thin sheets. The measurement of the Hall coefficient for a bar of iron was accordingly undertaken. The dimensions of this bar were 2.005 cm by 1.050 cm by 11 cm. It was forged out of electrolytic iron to which 0.2 percent of manganese was added to make it forgeable. The bar was then carefully machined and filed to the dimensions given. The iron was prepared and forged by the Westinghouse Research Laboratories. Although this particular sample was not analysed, another sample prepared in the same

[1] J. C. Steinberg, Phys. Rev. **21**, 22 (1923).
[2] W. van B. Roberts, Phys. Rev. **24**, 532 (1924).

way, except that no manganese was added, contained less than 0.06 percent of all impurities.

Method of Measurement

(a) *Magnetization curve.* Since a bar of iron was used, the usual method of determining the *B-vs-H* curve could be employed. The bar was placed in a magnetic circuit with a search coil wrapped around it near the center. The search coil was connected in series with a ballistic galvanometer and the secondary of a standardizing air-core solenoid. This made the determination of the absolute values of magnetic induction quite simple. Readings on the bar were made by reversing a given magnetizing current after the bar had been first completely demagnetized. No attempt was made to obtain the absolute value of the magnetic field strength H, and so a quantity proportional to the permeability was calculated by dividing the magnetic induction by the magnetizing current. However, since the balance of the magnetic circuit consisted of nearly pure soft iron of much larger cross-section than the bar under test, the true field H in the bar could be considered proportional to the magnetizing current without appreciable error.

(b) *Current density.* Measuring the Hall e.m.f. presented more difficulties. It was necessary to produce current densities comparable to those used by other investigators in their thin sheets and to have them perpendicular to the magnetic induction. Reference to Fig. 1 will show how this was accomplished. A current of 50 to 100 amperes from a storage battery was passed through the bar by means of the electrodes M, M', E, E'. By increasing the current through the outside electrodes, E, E', it was possible to make the lines 1-2-3 and 4-5-6 equipotentials, and thus insure sensibly uniform parallel lines of flow between the middle electrodes M, M'. To test for these equipotentials, one terminal of a galvanometer was connected to a fixed position on the iron bar and the other terminal was touched successively to the points 1, 2, 3, 4, 5, 6. The lengths of the leads to electrodes E, E' were adjusted until the readings taken at points 1, 2, 3 were equal to each other, as were also those taken at 4, 5, 6. After the final adjustment, the variation in either group of readings was less than 1 percent of the difference in readings between points 2 and 5. Therefore, neither of the lines 1-2-3 and 4-5-6 varied from equipotential lines by more than 1 percent of the potential difference between them, and the error in the current density at point O between M and M', calculated by assuming the current to flow in parallel lines between M and M', was no greater than 2 percent. Correction was made, of course, for the width of the slots between M and E.

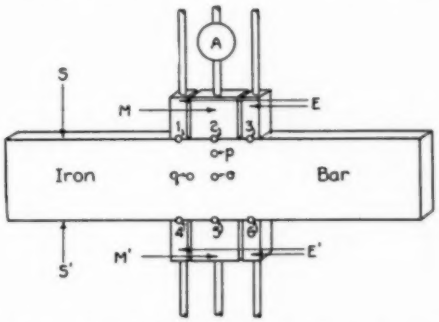


Fig. 1. Electrodes soldered in place to produce high uniform current density in iron bar.

(c) *Hall e.m.f.* The Hall e.m.f. was measured by means of a Wolff Thermokraftfrei Potentiometer and a Leeds and Northrup High Sensitivity galvanometer. The combination was capable of reading to 10^{-8} volts. Connections to the iron bar were made by means of two electrolytic iron contact screws which were pressed against opposite sides of the bar at point *O*. To test the accuracy of the current density adjustment described in (b) some readings were also made at points *p* and *q*. Since the Hall e.m.f. readings taken at these points fall on the same curve as those taken at *O*, the current was assumed to be uniform in this space.

The current between the electrodes and the magnetizing current were both allowed to become steady before readings were taken. Then the potential difference between the contact screws was measured. The magnetizing current was then reversed and the potential difference was measured again. The difference between these two potentiometer readings was twice the Hall e.m.f. No corrections were necessary for *IR* drops or thermoelectromotive forces since these would not change with the reversal of the magnetization. *This process was repeated many times, and at each reversal of the magnetizing current, the throw of the ballistic galvanometer was read, so, the Hall e.m.f. and the magnetic induction were both measured at the same time.* See Table I.

TABLE I. *Sample data giving Hall e.m.f. and magnetic induction.*

Magnetic induction = (59.56 − 47.07) 789 = 9850 gauss
Hall e.m.f. = 287.6/2 = 143.8 volts × 10^8

	Ballistic galvanometer readings (cm)		Potentiometer readings (volts × 10^8)		Differences (volts × 10^8)
1		47.1		974	
2	59.6		1262		288
3		47.0		974	287
4	59.7		1260		286
5		47.05		974	289
6	59.5		1266		287
7		47.1		983	285
8	59.6		1270		287
9		47.05		982	283
10	59.5		1260		286
11		47.05		965	290
12	59.5		1250		292
13		47.05		951	286
14	59.5		1223		286
15		47.1		923	290
16	59.6		1203		291
17				901	288
18			1175		288
19				872	
Ave.	59.56	47.07			287.6

(d) *Corrections.* All values plotted on the curve in Fig. 2 have been corrected to a current density of 24.7 amps. per cm^2 and to a temperature of 26°C. For the temperature correction, a coefficient of 1.36 percent per °C, given by A. W. Smith[3] was used. This coefficient may not be very ac-

[3] A. W. Smith, Phys. Rev. 30, 1 (1910).

curate for the iron used, but the important points were all taken so close to 26°C that the correction was negligible.

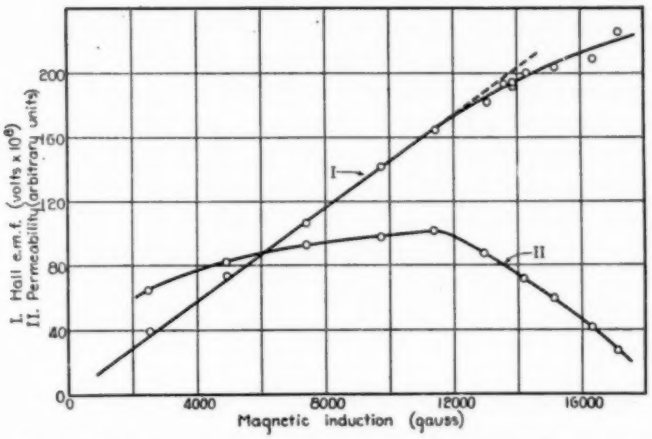


Fig. 2. Curves showing Hall e.m.f. and permeability in bar of electrolytic iron.

RESULTS

(a) *Hall e.m.f. and permeability.* It will be seen from the curves in Fig. 2 that the Hall e.m.f. increased linearly with the magnetic induction up to approximately 12,000 gauss. It will also be noticed that the permeability curve reaches its maximum at approximately the same point, namely 12,000 gauss. Therefore, the condition of the iron which causes the break from linear relation in the Hall effect is apparently the same as that which causes maximum permeability.

(b) *Hall coefficient.* The Hall coefficient R for this bar at 26°C was calculated from the formula[4] $E=RBib$ using the slope of the straight line part of the curve in Fig. 2 for the ratio E/B. Its value was 0.0055 c.g.s. electro-magnetic units, and the error is less than 3 percent. A. W. Smith[3] found a value of 0.0066 c.g.s. e.m.u. for a sheet of electrolytic iron which he measured in 1910. Since the value of the coefficient has been shown to be greatly influenced by the size of the crystals in the material and by slight impurities, the difference between these two values is not surprising. If, however, the value of H had been used in the calculation instead of B, the coefficient would not be constant, and its value would be increased several thousand fold. This would place its value above that for bismuth.

[4] It should be noticed (Fig. 2) that the Hall e.m.f. is plotted against magnetic induction B rather than field strength H. In all previous experiments on the Hall effect the field strength was measured in the space outside the thin sheet of material, which obviously gave the induction inside the sheet. Most investigators have recognized this fact, but it is the belief of the author that the use of H in the generally accepted formula $E=RHI/t$ has been misleading to many and should be replaced by B. The author believes that the formula should be written $E=RBib$ since the effect depends primarily upon the current density i rather than the total current I. Here $i=I/bt$, where b is the width of the strip in the direction in which the Hall e.m.f. is measured.

(c) *Hysteresis loop.* A set of measurements was made when the iron was taken through a number of complete hysteresis loops by closing the magnetizing circuit first in one direction, then opening it, then closing it in the opposite direction, and then opening it again. Each time the magnetizing current was made or broken, the throw of the ballistic galvanometer was read and a potentiometer reading was taken. From these readings, four points on the hysteresis loop were plotted, and the corresponding values of Hall e.m.f. were plotted upon the same sheet. The resulting curve for the Hall e.m.f. was another hysteresis loop which was proportional to the first, within the limits of observational error. The accuracy of these readings was little better than 10 percent on account of the difficulty in keeping conditions constant during the time required for completing each loop, but the results show quite definitely that there is a Hall effect due to the residual magnetization of the iron.

Conclusions

In the present work a method has been devised to measure both the Hall e.m.f. and the magnetic induction in the same piece of material at the same time. It is shown (Fig. 2) that in the specimen of electrolytic iron used the maximum on the permeability curve and the break from the straight line on the Hall e.m.f. curve occur at the same value of magnetic induction. It is also shown that a Hall e.m.f. occurs due to residual magnetism which is approximately the same as that due to a corresponding induction on the normal magnetization curve. The Hall coefficient was found to agree within 20 percent of that given by A. W. Smith[3] in 1910 for electrolytic iron. This discrepancy might easily be accounted for by differences in purity or in treatment of the two samples of iron.

The following conclusions can then be drawn for this specimen of electrolytic iron:

(a) The linear relation between the Hall e.m.f. and the magnetic induction breaks down where the permeability reaches its maximum value.

(b) A Hall e.m.f. is produced by the residual magnetism which is approximately the same as that produced by a corresponding value of magnetic induction on the normal magnetization curve.

(c) The Hall coefficient is of the same order of magnitude in the bar as in the thin sheets providing the value of B be used in the calculation instead of the value of H.

The author wishes to thank Dr. J. J. Weigle and Professor A. G. Worthing for their valuable suggestions and criticisms. He also wishes to acknowledge his indebtedness to the members of the Physics Department of Carnegie Institute of Technology and to the Westinghouse Research Laboratories for furnishing the iron bar.

University of Pittsburgh and Carnegie Institute of Technology,
Pittsburgh, Pennsylvania,
July 23, 1927.

THE TEMPERATURE COEFFICIENT OF QUARTZ CRYSTAL OSCILLATORS

By Roger S. Strout

Abstract

The change of frequency with temperature of a quartz crystal plate 1.8×1.8×0.11 cm, vibrating in a direction normal to its faces with a frequency of 2700 KC, was determined at various temperatures. A second oscillating plate was used as a fixed frequency, while the heterodyne note was heard with a receiving set. This second plate was maintained at, or near, room temperature, and was reground to an appropriate frequency for each determination. The temperature coefficient of frequency was found to decrease linearly from 22.7 parts per million per degree at 65°C to 1.6 parts per million per degree at −189°C.

SINCE quartz crystal plates were first used as resonators and oscillators it has been recognized that they have a negative temperature coefficient of frequency. Cady[1] states that, "Quartz plates vibrating under the longitudinal effect in a direction normal to their faces usually have a coefficient of about twenty parts per million." Powers,[2] using the transverse effect in a resonator of 91KC determined its coefficient using a temperature range of 20 to 110°C. In neither case was any attempt made to show that the coefficient did not change with temperature. The following work was undertaken to test its constancy.

Of the three possible modes of oscillation, that in a direction normal to the faces of the plate was chosen for two reasons. First, by its use the highest frequencies are attainable, thus giving a large difference of frequency for a given temperature change. Second, this mode of oscillation is in considerable use commercially and the results would be of greater practical value.

A slab was sawed from a quartz crystal in the well known Curie 3 or "zero angle" cut,[3] and from it two plates 1.8×1.8×0.11 cm were cut and ground. These plates were mounted in waterproof holders in a horizontal position with light upper electrodes resting upon them. This type of holder was selected as being the least affected by temperature changes. The mounted plates were then connected to conventional oscillator circuits in the grid to filament position, with a grid leak to provide the proper grid potential. The two independent oscillators were placed about a meter apart and about equally distant from a regenerative receiving set of appropriate range.

Of the two plates, the one giving the highest frequency was selected as the test plate. This plate (A) in its container, was immersed in a Thermos-bottle water-bath at the highest temperature at which tests were to be made

[1] W. G. Cady, Jour. Opt. Soc. Am. **10**, 475 (1925).
[2] W. F. Powers, Phys. Rev. **23**, 783 (1924).
[3] A. Crossley, Proc. I. R. E. **15**, 9 (1927).

and the circuit adjusted for best operation. The second plate (*B*) was operated in the same manner, but in a water-bath at room temperature. The difference in frequency of the two oscillators could then be heard as a loud heterodyne note in the phones of the receiving set. Then by repeated trials plate *B* was reground until its frequency, at room temperature, differed by less than 200 cycles from that of the test plate *A* when *A* was operating at the temperature at which the determination was to be made. The temperature of plate *B* was then altered by means of its water-bath, until the heterodyne note reached the lower limit of audibility. Then with the receiver oscillating at a frequency not greatly different from that of the quartz plates, two heterodyne notes were heard in the phones, differing slightly in frequency. The temperature of water-bath *B* was then further changed until these two heterodyne notes were brought to zero beat. Any change in the tuning of the receiver altered both heterodyne notes the same amount and did not alter their difference. Zero-beat adjustment having been secured, the receiver was rendered non-oscillating and the temperature of bath *A* increased. A single note, whose frequency increased with the temperature change, was then heard in the phones. The temperature was increased until the note came to zero-beat with a 192-cycle tuning fork, the temperature change being noted on a Beckmann thermometer. The water-bath *A* was then cooled until zero-beat between the quartz plates themselves was again secured, the temperature change being again noted. At least five such readings were taken and the average change of frequency per degree change of temperature was recorded as the rate for the middle of the temperature range. The test plate *A* was then cooled to the temperature at which it was desired to make the next determination and plate *B* was again reground to operate at room temperature and give zero-beat with *A* as before. The process was then repeated and another value recorded.

The zero-beat adjustment of frequency is not permanent, because of unavoidable slight changes in the circuit constants, particularly in the three-electrode tubes. This causes a slight wandering of the output frequency. After the tubes were warm the increase in frequency of one oscillator over the other due to this wandering seldom exceeded one cycle in two seconds, although the plates were oscillating at approximatly 2700KC. Since the frequency of the two circuits wandered independently and in either direction, an average of several readings tended to reduce this error. Any radical change of frequency was manifested by a failure to obtain zero-beat at approximately the same temperature after each pair of readings. The operation of plate *B* at approximately room temperature made this check possible, as its temperature would not vary over one-hundredth of a degree in the time required to take a pair of readings. No tendency of the crystal-controlled oscillators to pull into synchronism, as zero-beat was approached, could be detected, even when the inductances were placed only one foot apart. The above method was used at 65°C and 23°C and, with the substitution of an alcohol bath, at −27°C.

For the lower temperatures the change from melting methyl alcohol to melting carbon disulphide and from liquid oxygen to fresh liquid air gave convenient temperature ranges. For the latter range it was necessary to operate the quartz plate in an oxygen-free atmosphere, as otherwise the oxygen in the container condensed and caused the plate to stop oscillating. In each case plate B was ground to give zero-beat with plate A when A was in one refrigerant, and the subsequent change of frequency when the other refrigerant was substituted was determined by comparing the note in the phones with a calibrated oscillator or tone wheel. The probable percentage error of this method is much greater than that of the first method, and is increased with decreasing temperature, chiefly because of errors in the measurement of both absolute temperature and temperature changes. As the coefficient itself decreases rapidly with temperature this is not of great importance, since the actual error in cycles change per degree remains sensibly constant.

TABLE I. *Natural period of plate 2700KC*

Temperature	Cycles change per degree	Coefficient (Parts per million)
65°C	61.3±0.8	22.7
23	52.6±0.5	19.5
−27	40.3±1.5	14.9
−105	23.4±2.0	8.7
−189	4.3±0.5	1.6

Plotting the coefficient against temperature the results fall on a straight line within the limit of accuracy of the experiment. Several tests on plate B gave in each case slightly larger coefficients, but indicated a line on the graph parallel to the line for plate A. The small difference in coefficient could be accounted for by differences in surface-figure of the two plates, since they were not made optically plane-parallel. It was found possible to alter the temperature coefficient by as much as ten percent by inaccurate surface grinding, without apparently affecting the stability of oscillation.

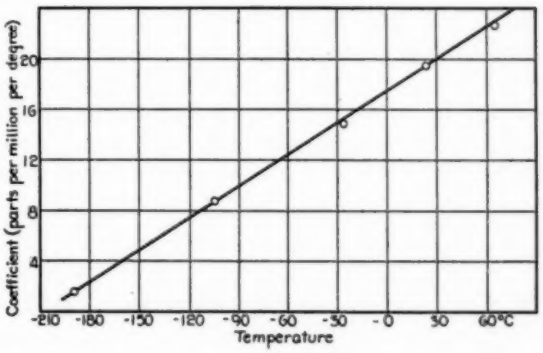


Fig. 1. Temperature coefficient of frequency of quartz oscillator, natural frequency 2700 KC.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
December, 1927.*

* Received August 21, 1928. Ed.

VISIBLE RADIATION CHARACTERISTICS OF INCANDESCENT OXIDES

By Marcella Lindeman Phillips

Abstract

Energy radiated in the visible part of the spectrum of various oxides and their mixtures when heated to red brightness temperatures between 1400° and 2000°K by means of cathode-ray bombardment, and gas-air and oxy-gas flames was measured by an optical pyrometric method. The oxides investigated were urania, ceria, lanthana, neodymia, erbia, yttria, zirconia, thoria, alumina, beryllia, magnesia, and mixtures of thoria with one percent ceria (the Welsbach mantle mixture), one percent and less of urania, one percent neodymia, and one percent manganese oxide. These were either pressed or fused to insure good surface conditions. In general, linear relations were found between the logarithm of the red-blue intensity ratio and the reciprocal of the brightness temperature, and between the logarithm of the candles emitted per unit surface area and the logarithm of the brightness temperature. Different modes of heating gave different radiation curves for the same oxide. Tables are given of the candles per square centimeter and the relative blue brightness for red brightness temperatures of 1400, 1500, 1600, 1700, 1800, 1900, and 2000°K.

INVESTIGATION of the visible radiation of certain oxides, with reference to their possible use as illuminants, has extended over a period of more than a century, but few quantitative results have been published, the most extensive researches being those due to Nichols and Howes,[1] and to Ives, Kingsbury and Karrer.[2] The former investigation, a part of which is concerned only with low temperatures of incandescence consists of a comparison of the radiation of the oxide under test with that of uranium oxide, both oxides being heated in adjacent parts of a flame, assuming the uranium oxide to radiate like a "black body" and to be at the same temperature as the oxide under test. It is shown below that this assumption is very doubtful. The latter research was upon oxides made up into gas-mantle form, the results given being thus characteristic not only of the oxides, but also of the degree of roughness of the mantle surfaces.

The work presented in this paper is an investigation of the visible radiation characteristics of various oxides and oxide mixtures when heated by cathode-ray bombardment, gas-air and oxy-gas flames, to brightness temperatures ($\lambda = 0.665\mu$) from about 1400 to 2000°K.

An optical pyrometric method of observation was used, measurements of the brightness of the oxide under test being made with a disappearing-filament type of pyrometer, equipped successively with red (effective $\lambda = 0.665\mu$) and blue (effective $\lambda = 0.467\mu$) screens, from which the red brightness temperature and the ratio of red to blue intensity ratio were determined, and with a combination of red and green screens having an

[1] Nichols and Howe, Phys. Rev. **19**, 300 (1922).

[2] Ives, Kingsbury and Karrer, Journ. Franklin Inst. **186**, 401 (1918).

effective wave-length approximately equal to the Crova wave-length, from which the candles emitted per square centimeter of surface were determined.

The pyrometer used was calibrated by comparison with a standard tungsten lamp previously matched with a "black body" furnace at the melting points of gold and palladium in this laboratory. Matches were made, with the different screens, at these fixed points of the standard lamp, the calibration being extended to other temperatures by the use of rotating sectors of known transmission. A precision of about 0.1 percent in brightness temperature was obtainable for a single setting on a steady source of light such as a tungsten lamp. This precision is somewhat better than that claimed for the observations on oxides, since in the latter case, the light source was not always constant, and it was sometimes necessary to make hurried settings. An approximately average value of the precision here attained is 1.0 percent, although it is to be understood that the precision varied with the brightness of the source and the mode of heating. For oxy-gas heating it was better than the average value given, while for cathode-ray and gas-air heating, it was somewhat worse. Wide deviations from this average will be noted in the discussion of the results.

Ordinary gas-air burners, equipped with valves regulating the gas pressures, were used in flame heating. The oxides were kept in the oxidizing part of the flame.

A cold cathode discharge tube, connected through a long capillary to an oxygen tank, was used in studying the oxides under cathode-ray bombardment. The oxide, mounted in a nickel button, served as the anode, and was viewed through a window at the end of a long arm of the tube. With the window thus at some distance from the hot circle the error due to blackening of the tube during operation was greatly reduced.

The oxides used, unless otherwise stated, were in as pure a state as could be obtained, and were either pressed as compactly as possible in a hydraulic press, or fused to insure a smooth surface. The samples of the fused oxides were prepared by melting them in an atomic hydrogen arc by C. W. Hewlett of the General Electric Company Laboratory in Schenectady. Due to the fragility of the pressed oxides, fused oxides were used when possible.

In general, a linear relation was found between the logarithm of the brightness in candles per square centimeter and the logarithm of the red brightness temperature, and between the reciprocal of the red brightness temperature and the logarithm of the red-blue intensity ratio, these curves differing with the different oxides, and with different modes of heating for the same oxide.

The accompanying table gives values of relative brightness in the blue part of the spectrum and the total brightness in candles per square centimeter at several red brightness temperatures for different oxides, this method of presenting the results of the investigation being chosen in order to conserve space. The blue brightnesses are in terms of the blue brightness of the black body at the melting point of palladium taken as unity. A very large number of observations were made in each case, covering the temperature ranges indicated.

Uranium oxide. This oxide is of particular interest, since it was used as a standard source of comparison in the work of Nichols and Howes, and since it was suggested as a substitute for ceria in the Welsbach mantle mixture by Ives, Kingsbury, and Karrer. The samples used were pressed, but the surface became rough at high temperatures because of evaporation of the

TABLE I. *Relative blue brightness, B, and brightness in candles per cm², C, of some incandescent oxides at various red (0.665μ) brightness temperatures, S_R.*

Material	S_R=1400 B	C	1500 B	C	1600 B	C	1700 B	C	1800 B	C	1900 B	C	2000 B	C
Black body	.0061	.26	.026	.79	.091	2.1	.27	5.0	.74	11.3	1.80	23.0	3.9	44.0
Tungsten	.0091	.26	.038	.84	.134	2.3	.41	5.9	1.11	14.4	2.7	33.0	6.3	74.0
Urania (gas air and Oxy-gas)	.0066	.36	.028	1.02	.100	2.7	.31	6.6	.84	15.5	2.0	35.0	4.5	78.0
Ceria, Pure (Cat. ray)	.019*	.50	.0105	1.41	.299	3.7	1.02	9.4						
(Gas air)	.0063*		.029											
(Oxy-gas)	.0090	.41	.035	1.08	.113	2.7	.32	6.3	.83	14.1	1.90	31.0	4.0	62.0
Ceria, Yellow (Oxy-gas)	.0079	.36	.032	1.04	.109	2.8	.32	7.1	.85	17.1	2.0	40.0	4.0	88.0
Ceria, Brown (Oxy-gas)	.0089	.44	.033	1.15	.107	2.9	.30	6.7	.83	15.2	1.68	33.0	3.5	68.0
Oxides of Cerium Group (Oxy-gas)	.0071	.34	.031	.97	.109	2.5	.34	6.3	.92	14.7	2.3	33.0	5.0	71.0
Neodymia (Oxy-gas)	.0068	.44	.032	1.17	.107	2.9	.33	6.9	.92	15.3	2.3	33.0	5.0	64.0
Lanthana (Oxy-gas)	.0082	.42	.033	1.11	.113	2.8	.34	6.6	.89	15.0	2.1	33.0	4.5	64.0
Erbia (Oxy-gas)	.0122	.73	.047	1.71	.157	3.8	.45	8.1	1.17	16.6	2.7	33.0	5.6	63.0
Yttria, Pure (Oxy-gas)	.0174	.43	.067	1.18	.216	3.0	.61	7.3	1.56	17.2	3.6	32.0	7.3	63.0
Yttria, 95% pure, (Oxy-gas)	.0118	.45	.047	1.20	.157	3.0	.46	7.3	1.19	16.6	2.8	36.0	5.9	75.0
Zirconia (Cat. ray)		.37	.035	.74	.187	1.94	.53	4.8	.89	11.3				
Zirconia (gas air)	.0064	.38	.030	1.07	.096	2.9	.41	7.5						
(Oxy-gas)	.0148	.38	.058	.73	.192	1.66	.55	3.6	1.43	7.6	3.3	15.3	7.0	30.0
Thoria (Cat. ray)		.36		.89	.275	2.3	.90	6.5	2.5		5.2		7.7	
(Gas air	.0089	.43	.039	1.23	.146	3.3		8.5						
(Oxy-gas)	.0182	.58	.033	1.44	.207	3.4	.56	7.5	1.40	15.9	3.1	32.0	6.3	63.0
Alumina (Cat. ray)	.026	.80	.23	2.1	.738	4.9	2.0	11.2	5.1	23.0	11.6	51.0		
(Gas air)	.038	.58	.123	1.13	.346	2.1	.86	3.8						
(Oxy-gas)	.0174	.57	.076	1.45	.280	3.8	.87	9.4	2.5	22.0	6.1	49.0	13.6	103.0
Beryllia (Cat. ray)	.060	.53	.23	.98	.738	1.73	2.1	3.0	5.3		12.1		25.0	
(Gas air)	.0068	.54	.030	1.32	.107		.33							
(Oxy-gas)	.0196	.61	.086	1.62	.317	4.1	.99	9.7	2.8	22.0	6.9	49.0	15.4	104.0
Magnesia (Cat. ray)	.071	.85	.30	2.2	1.07	5.3	3.2	12.2		27.0		57.0		
(Gas air)	.021	.191	.089	.62	.289	1.95	.85	6.0						
(Oxy-gas)	.0187	1.05	.21	2.4	.559	5.2	1.31	11.0	2.8	22.0	5.6	43.0	10.2	79.0
Thoria, 1% Ceria (Oxy-gas)	.020	.54	.078	1.45	.249	3.6	.70	8.6	1.71	19.3	4.1	43.0	8.4	90.0
Thoria, 1% Urania (Oxy-gas)	.0173	.48	.069	1.33	.231	3.4	.67	8.3	1.77	19.3	4.1	44.0	8.7	93.0
Thoria, trace Urania (Oxy-gas)	.0131	.48	.059	1.33	.216	3.4	.68	8.3	1.93	19.3	4.8	44.0	10.5	93.0
Thoria, 1% Neodymia (Oxy-gas)	.0117	.60	.046	1.43	.152	3.3	.43	7.1	1.14	14.7	2.6	29.0	5.5	56.0
Thoria, 1% Manganese Oxide (Oxy-gas)	.0083	.44	.035	1.13	.122	2.7	.37	6.1	1.01	13.3	2.4	28.0	5.3	56.0

*S_R=1429°K

oxide. This would tend to make the radiation curves approximate more nearly those of a "black body," although the fact that the curves are very close to those of a "black body" at low temperatures indicates that the radiation is similar, although not identical. High infra-red emission made it difficult to heat in the gas-air flame, but the few observations made indicated

that the curves for this form of heating were identical with those obtained with oxy-gas flames.

Cerium oxide. Pressed samples were used, since those fused in the atomic hydrogen arc were reduced, and could not be brought back to their original state of oxidation, as could the other oxides, by heating in an oxidizing flame over any reasonable length of time. The pure oxide (almost white in color) gave a brilliant yellow radiation, probably luminescence, when heated in a flame, at a temperature far below that of red incandescence. In the discharge tube a bright greenish-blue radiation was emitted at temperatures below red incandescence, a property shared with all the other oxides investigated.

The radiation curves obtained are similar to those of urania and a "black body" for oxy-gas and gas-air flame heating although quite different for heating by cathode rays. Difficulty of heating to high temperatures by a gas-air flame indicated rather large infra-red emission.

Curves were also obtained showing the effect of different amounts of impurities (probably praseodymium oxide) on the radiation curves.

Lanthanum oxide. The samples were prepared by ignition of the hydroxide, and the resulting powder was pressed into a flat button. They were particularly fragile and could not be used for successive heating, for after heating and subsequent cooling, they increased greatly in volume, then crumbled into powder. The radiation is similar to that for urania and ceria.

Neodymium oxide. The samples were prepared by ignition of the hydroxide, and were dark brown at room temperature. This brown oxide is often referred to as a hydroxide, but since it remained unchanged in color after prolonged heating and fusion this seems unlikely. The majority of observations were taken on pressed samples. This oxide affords a good illustration of change of radiation with temperature since, just before arriving at red incandescence, it gives off a brilliant blue light, when heated in flames.

Erbium oxide. Observations were made on pressed samples. This oxide differs appreciably in its radiation from those previously discussed, in possessing far greater values of candles per square centimeter and higher values of blue brightness for a given red brightness temperature.

Yttrium oxide. Observations were made on the purest yttria obtainable and on yttria possessing five percent of unknown impurities. The great difference between the two curves obtained illustrates the enormous effect of a small amount of impurity and the importance of having the samples as pure as possible. Both samples were pressed.

Zirconium oxide. Both fused and pressed samples were used, no difference between them being noted for similar modes of heating. During the course of the observations made with cathode-ray heating, it was found that the radiation curves approached those of a "black body" for high values of red brightness temperature due to the partial reduction by the cathode rays, and consequent blackening of the oxide.

Easy loss of oxygen at high temperatures is characteristic of all the oxides investigated. Even when mounted in platinum, sealed into an evacuated bulb and heated with induced high frequency current they became blackened,

pronounced loss of oxygen taking place at temperatures at which the blue glow emitted before red incandescence was reached. This is good evidence, in the absence of any other, that the blue glow is luminescence, i.e., radiation at a given wave-length or wave-lengths in excess of that given off by a "black body" at the same temperature, and probably due to the energy liberated by this chemical dissociation or its reversal. Computations made in a few cases where the heat of dissociation is known showed that this should account directly for light in the ultra-violet part of the spectrum, and that the blue glow is very likely a fluorescence or phosphorescence phenomenon. It is, however, possible that the dissociation process responsible for the glow is only part of that for which computations were carried out, since many of the substances possess stable suboxides, and there are indications of many unstable forms of suboxidation for which the heats of dissociation are unknown.

Thorium oxide. Both fused and pressed samples were observed. Cathode rays tended to reduce this oxide, as in the case of zirconia. This oxide is of particular interest since it forms the basis of mixtures discussed later.

Aluminum oxide. This and the following oxides are notable for their extraordinarily large blue brightness at the red brightness temperature at which these oxides were studied. Both fused and pressed samples of alumina were used. A bluish-white light was emitted at very low temperatures under flame heating. Ease of heating to incandescence in flames indicates very low infra-red emission.

Beryllium oxide. Both fused and pressed samples were used. As in the case of alumina, the light given off at low temperatures with flame heating is bluish-white. Difficulty of heating in gas-air flames indicates large infra-red emission. At the highest temperatures reached by oxy-gas flame heating, boiling of the oxide was observed. At the lowest temperatures observed with gas-air heating the precision was very low. Consistent observations could be made while the temperature was maintained constant, but upon changing the temperature, then returning to the first temperature the observations gave different results from the first. The data given represents the mean of all the observations taken. No consistent variation with the history of the sample was noted, but it is possible that this is a luminescence phenomenon and is dependent upon its oxidation.

Magnesium oxide. Both fused and pressed samples were used. A bluish-white light was emitted at low temperatures of flame heating as in the case of beryllia, and, even more pronounced than in the case of beryllia, the precision of measurement under gas-air heating and also cathode-ray bombardment was very low, although consistent readings could be taken when the sample was maintained at constant temperature. Variations as large as 10 percent in the blue brightness were observed upon returning to a given red brightness temperature, although the curves for the variation of candles/sq. cm with the red brightness temperature were fairly consistent.

Thoria-ceria mixture. A 1 percent ceria-99 percent thoria (by weight) mixture was prepared by forming a mixed solution of the salts, evaporating to dryness and heating to form the oxides. The percentage was determined,

as in the following mixtures, by weighing the oxide formed from a known volume of each solution before mixing. This process was used in forming all the mixtures observed. The formation of thoria in this manner is accompanied by a great increase in volume, resulting in a spongy tenacious structure. This is the method used in the formation of Welsbach gas mantles, the percentage used here being the "Welsbach Mixture."

The samples used for this and the following mixtures were pressed,since the surface when formed as in the mantle is very irregular. It was found that the radiation curves for the mixture did not lie, as one might suppose, between those of ceria and thoria, but show much greater values of candles per square centimeter and, proportionally, much more blue light for a given red brightness temperature than thoria alone. This is in accordance with the results of previous observers. The chief theories brought to account for this have been:

(1) That this mixture represents a chemical compound or stable solution having individual radiation characteristics.

(2) That ceria acts as a "catalytic agent" in oscillatory oxidation processes resulting in increased luminescence, and

(3) (Perhaps the most commonly held theory) That ceria is a good selective radiator, but because of its good radiation is unable, by itself,to reach a high temperature in a flame, whereas thoria is a poor, non-selective radiator; able, on account of its poor radiation, to reach a very high temperature, the mixture owes its effectiveness to the fact that the poor radiation of thoria enables the ceria to reach a high temperature where it emits light largely in the visible spectrum.

Without knowledge of the true temperatures, very little can be said about the cause for the difference in radiation. It may be observed here, however, than thoria is a much more "selective" radiator than ceria in the visible region of the spectrum. Relative case of heating with flames indicated that it had much lower infra-red emission. The facts that the blue glow at low temperatures is accompanied by pronounced loss of oxygen, and that, of all the oxides investigated, ceria showed the greatest tendency toward reduction, give weight to the second theory.

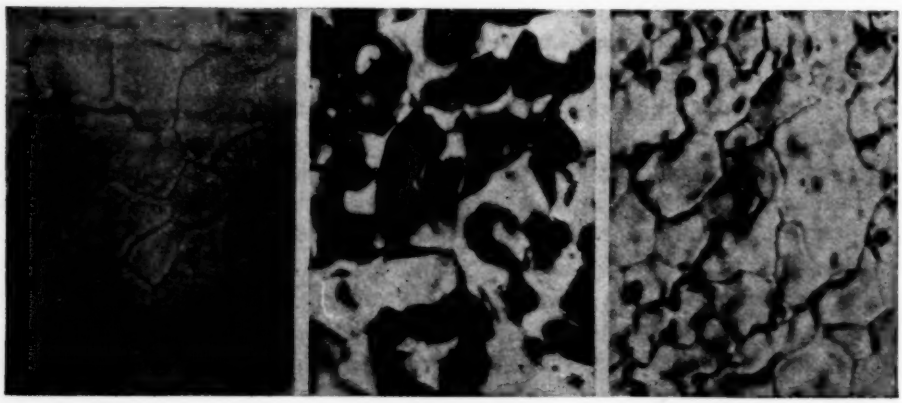
Thoria-urania mixtures. Since urania, like ceria, has radiation curves approximating those of a "black body," a one percent (by weight) mixture with thoria was similarly observed, as well as one having a much lower percentage of urania. When heating uranium nitride in a crucible to form the oxide, it was found that the urania penetrated into the porcelain, coloring it olive-green. Subsequent heating of thorium nitrate in the same crucible removed the stain, the urania being dissolved in the thoria. Before complete oxidation the uranium oxide is a deep reddish-orange color. The one percent solution was a rather bright orange, while the last solution was a very light orange, therefore the "trace" of urania was estimated as being less than 0.1 percent, by weight, of the mixture.

It may be noted that these mixtures behave, in general, like the thoria-ceria mixture. Since the evaporation of urania, when heated alone, is rather

large and results in a slightly roughened surface, it is possible that the radiation curves for both urania and its mixtures as given here are nearer to those of a "black body" than they should be to typify their characteristic radiations.

Thoria-neodymia mixture. It was thought that mixtures of thoria and neodymia would resemble those of thoria with urania and ceria, since the radiation curves of urania, ceria, and neodymia are similar. This was not found to be the case with the mixture observed.

Thoria-manganese oxide. Mixtures of thoria with manganese oxide were suggested in the paper of Ives, Kingsbury, and Karrer as being of the type of the "Welsbach Mixture." In the present work it was found impossible to determine the radiation curves of the oxide alone, since it melted at a rather low temperature. The mixture, initially colored dark brown, whitened



I II III

Fig. 1. Microphotograph I. Surface of tungsten filament containing 15% zirconia, after heating to brightness temperature of 1800°. 750×. Microphotograph II. Surface of tungsten filament containing 15% zirconia, after heating to brightness temperature of 2500°. 750×. Microphotograph III. Surface of tungsten filament after prolonged heating at high temperatures 750×.

upon heating, so that the radiation curves here given are most probably those for slightly roughened thoria. That they lie between those for thoria and for a "black body" tends to confirm this idea, and shows the importance of having as smooth a surface as possible when making observations of this type.

A very good illustration of the importance of surface conditions in studying characteristic radiations of any kind was given by a preliminary experiment to those discussed above. Thinking that zirconia, reputed to radiate selectively for the most part in the visible region, but very difficult to use practically, might furnish a good form of illumination when combined with tungsten, lamp filaments were made of powdered tungsten mixed with zirconia, then squirted and sintered. Observations were made on those, but

the precision was not satisfactory because of the roughness of the surface. After polishing, the precision was the same as that obtained for good tungsten filaments at low temperatures, the radiation characteristics being very slightly better. At brightness temperatures of about 1800° a decrease in precision was noted which became progressively greater with increasing temperature, the radiation curve more nearly approximating that of a "black body." Microphotographic inspection revealed that the surface had become pitted as a result of the evaporation of the zirconia (most probably reduced to zirconium on heating).

The amount of roughening is shown in the accompanying microphotographs. After polishing, the surface appeared perfectly smooth at 1500x, and highly reflective to the naked eye. After heating to about 1800° brightness temperature it still appeared highly reflective, but under the microscope revealed small pits at the boundaries of the crystallites of tungsten, as shown in Microphotograph I. After further heating, the surface looked dull, although smooth, to the naked eye, but under the microscope presented the very roughened appearance shown in Microphotograph II. Prolonged heating of tungsten filaments resulted in no appreciable loss of precision. The only roughening experienced in this case is that of "heat etching" due to the differential evaporation along different crystalline planes, shown in Microphotograph III.

The author wishes to express her appreciation to the staff of the Research Laboratory at Nela Park for their interest and assistance in the present work, and especially to Dr. W. E. Forsythe, who suggested the problem, and under whose direction the work was carried out.

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BOOK REVIEWS

Physik der Gasentladungen. RUDOLPH SEELIGER. Pp. 423, 5 tables, 184 figs. Johann Ambrosius Barth, Leipzig, 1927. Price 24 R. M. bound, 22 R. M. unbound.

This admirably written book is a comprehensive and well organized review of the subject of electrical discharge in gases in the light of the most recent developments in theory and experimental technique, with particular reference to the corona, spark, glow and arc types of discharge. The author is perhaps the leading student and critic in this field and the researches of himself and his students, directed at strategic problems, are responsible for some of the most valuable parts of the book. At the same time the discussion of recent researches by other investigators is very fair. Altogether the book gives a unified view of the present state of knowledge in this field, together with a keen analysis of outstanding difficulties in the theories.

Chapters 1, 2 and 3 deal with fundamental concepts: "The Conductivity of Gases," "The Theory of Ions" and "The Kinetics of Charge-Carriers." Here are discussed current limitation by space charge, free paths, critical potentials, probabilities of excitation and ionization, collisions of the second kind, thermal and impact ionization, secondary emission, the theory and use of exploring electrodes, etc. Chapter 4 deals with characteristics common to all self-maintaining discharges, the differentiation between different types, phenomena of striking, stability static and dynamical characteristics, etc. Chapters 5 and 6 deal with the phenomena and the theory of the "Townsend" discharge (in which there is exponential increase of ionization by electron impact, but no space charge sheath at the cathode). Influence of electrode form, nature of gas and corona loss are discussed and Townsend's theory is extended to take approximate account of distortion of the field by space charge. Chapters 7 and 8 deal descriptively with the glow discharge and the arc, respectively. Chapter 9 deals with the theories of discharge types and is probably the most interesting chapter in the book. Particular emphasis is given to the role of space charge. Theories of Guntherschulze, Holm, Schottky, Compton, Langmuir and others are critically discussed.

The book is attractively printed, the illustrations are excellent and the whole work gives the impression of thoroughness, carefulness and good judgment. References and notes are assembled in the rear of the book. There is no attempt to give a complete bibliography,—a lack which is not serious in view of the recent excellent bibliographies on this subject in Vol. 14 of the new Geiger and Scheel Handbuch der Physik.

K. T. COMPTON